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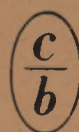
May, 1995

LITHOLOGY AND MINERAL RESOURCES

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LOCAL CARBONATIZATION OF WHITE SEA SEDIMENTS (CONCEPT OF MICROBIOLOGICAL FORMATION)

A. R. Geptner, B. G. Pokrovskii, T. A. Sadchikova,
L. D. Sulerzhitskii, and A. G. Chernyakhovskii*

UDC 552.14:552.54

This article considers peculiarities of the morphology, microstructure, and material composition of Holocene gennoishes (distinctive formations thought to be pseudomorphs of calcite after gaylussite) from litoral sediments of the White Sea. The authors investigated in detail the interrelation of gennoishes and the concretions sealing them up, with the surrounding sediments. In the structure of gennoishes, they established seven microstructural types of calcite segregations and investigated their peculiarities and the sequence of their formation. The isotopic composition of carbon in the calcite of gennoishes and concretions differs little from or is identical to modern formations of hexahydrate calcium carbonate (ikaite). The probable mechanism of formation and the possibility of bacterial origin of the gennoishes' and concretions' carbonate are discussed.

In the territory of Russia, a site of whimsical carbonate formations located in White Sea sediments has been known for about 150 years. These are so-called "White Sea horns," which are found in large numbers at the mouth of the Olenitsa River (Terskii coast of the Kola peninsula). Morphologically, "White Sea horns" are divided into two groups: concretions, and crystallike formations known in the literature as gennoishas or glendonites. Among the variously shaped manifestations of local carbonatization, gennoishas occupy a special place. These are quite unusual formations, outwardly reminiscent of large crystals or intergrowths of them, while their internal structure has nothing in common with the structure of crystals. The morphology and peculiarities of the internal structure of gennoishas are remarkably alike; they are preserved in deposits of various ages and conditions of formation without change for several hundreds of millions of years (from the Carboniferous to contemporary deposits). The most complete summary of data on gennoishas is given in [4]. Gennoishas have long been known in many regions of the globe, mainly in high latitudes of the Northern and Southern hemispheres. Available publications mostly relate to peculiarities of their morphology and, to a lesser degree, internal arrangement. The nature of gennoishas' interrelation with the material of surrounding rocks remains poorly studied. This circumstance has significantly affected formation of the idea of gennoishas' genesis as pseudomorphosis after some mineral (gaylussite, celestine, gypsum, glauberite, thenardite, aragonite) [4]. At present, many consider ikaite or hexahydrate calcium carbonate to be such a precursor mineral [17].

The need for detailed investigation of the conditions of formation of gennoishas is determined by their use as an indicator of low bottom temperatures [6, 13, 17]. However, this does not mean that low temperatures are the only or main factor in the appearance of such distinctive carbonate mineralization in terrigenous deposits. There are certain indications that the formation of ikaite, the precursor of gennoishas, is connected with the vigorous activity of microorganisms [17].

In contrast to older ones, White Sea gennoishas and concretions are unaffected by processes of secondary transformations. Therefore, many features of their primary structure, composition, and nature of their interrelation with the surrounding sediments, which accumulated in certain climatic and facial situations, can be studied most fully here, and the data obtained can serve as a good basis for genetic conclusions.

CONDITIONS OF OCCURRENCE OF CARBONATE FORMATIONS

The tidal flats in the region of the White Sea under consideration are a very gently sloping surface freed of water for many hundreds of meters at low tide. At maximum high tides, they are covered by a 2.5-3-m layer of water. As a result of wave activity, a complex system of shallow (10-20 cm), closed and flowing troughs or depressions is formed

*Deceased.

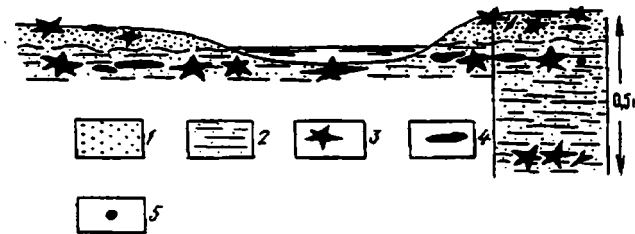


Fig. 1. Conditions of occurrence of gennoishas and concretions: 1) light-brown sands and silts; 2) dark-gray, pelitic silts; 3) gennoishas; 4) concretions; 5) location of specimen 90/86.

on the surface of the flat. The low places are separated by gently sloping, flat rises, on the surface of which wave ripples are very well expressed.

On the litoral, light-brown, pelitic sands and silts of various grain sizes lie at the surface, in places including fine pebbles and gravel (Fig. 1). The sands are horizontally bedded. The bedding is thin and lenticular, due to the alternation of sandy material of various grain sizes. In the sands, isolated specimens and accumulations of gennoishas, concretions (some of them with clear traces of wave action), scraps of plant organic matter, and entire shells of marine molluscs or fragments of them are found. Shells of foraminifers are found less often, and there are cell walls of diatoms. Coarse- and medium-grained terrigenous material is very slightly worked. The thickness of this layer near the shore varies from 5 to 20 cm, and where waves have washed out gentle depressions in the flat, the light-brown layer is absent. There, viscous, dark-gray, sandy-silty sediments with vague horizontal bedding that are exposed in test pits at a depth of about 0.5 m crop out to the surface. Approximately 500 m from the shore toward the sea, the thickness of the light-brown sands increases so much that the underlying dark-gray sediments already do not appear on the surface anywhere.

On the tidal flat at the mouth of the Olenitsa River, pebbles, large boulders, and blocks (up to 1.5 m across) bearing clear traces of glacial action (smoothed corners and faces, scars) are scattered in disarray. The base of the large boulders and blocks is buried in the dark-gray sediments.

Judging from a few test pits, gennoishas and concretions in the dark-gray sediments are found in their original position, concentrated at two levels (see Fig. 1). The upper one is located immediately under the layer of dark-brown sands; and the lower one, at a depth of 0.5 m from the surface. At this level, six multirayed gennoishas were found in one pit with an area of about 90 cm². The largest of them reaches 7 cm on its long axis.

In the lower part of the Olenitsa River valley, marine Holocene deposits compose the base of a series of alluvial terraces [5] (Fig. 2). In outward appearance, these deposits are similar to those that are exposed in test pits on the tidal flat. For example, the base of the 10-m terrace in the lower part is composed of horizontally bedded, viscous, dark-gray, sandy-silty sediments. Upward through the cross section, the number of layers enriched with sandy material gradually increases, and sandy-silty sediments are replaced by horizontally bedded sands of light-brown color. The thickness of the dark-gray sandy-silty deposits reaches 5 m; and of overlying sands, no more than 2.5-3 m. On the eroded surface of the sands lie pebble and sandy deposits of alluvium. In the same area of the river valley, the base of the 4- and 2-m terraces is composed only of dark-gray sands and silts. This is probably the only layer of marine deposits in which alluvium of various ages is embedded. Their foot is not revealed, but at the mouth of the river in the base of the floodplain light-brown (when wet), extremely sticky clays with unevenly distributed sandy and silty material and occasional boulders are exposed. In outward appearance, these deposits are reminiscent of moraine.

It should be emphasized that gennoishas and concretions washed out of the dark-gray marine sediments are found on the tidal flat only at the mouth of the Olenitsa River. The ranges of occurrence of gennoishas, concretions, and boulder-block material of eroded moraine coincide (see Fig. 2). Marine Holocene deposits composing the bases of river terraces here do not contain gennoishas or concretions.

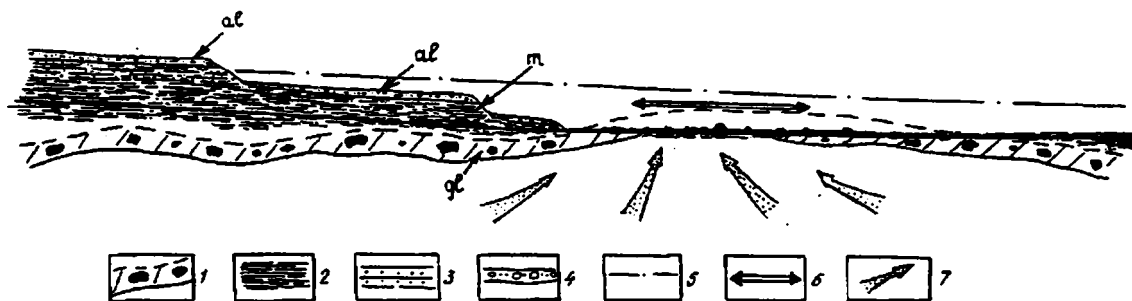


Fig. 2. Schematic geological profile along the line "lower course of the Olenitsa River – White Sea litoral:" 1) basic moraine; 2, 3) Holocene marine deposits (2 – dark-gray, silty, pelitic; 3 – light-brown sands and silts); 4) alluvial deposits: sands, pebble beds; 5) supposed roof of eroded marine Holocene deposits; 6) region of occurrence of gennoishas and concretions on the surface of litoral sediments; 7) supposed upflow of carbon-containing gases.

MATERIAL COMPOSITION OF SEDIMENTS SURROUNDING CARBONATE FORMATIONS

Gennoishas and carbonate concretions lie in terrigenous sediments formed mostly as a result of destruction and redeposition of moraine material. It was noted above that the sediments of the tidal flat differ in color through their cross section. The upper layer is composed of light-brown sands; and the lower one, of dark-gray (when wet), fine-grained sands and silts with varying content of pelite. The sediments of different color do not differ in composition of their clastic material. The main components, judging from the silty constituent, are quartz and potash feldspars, with a small admixture of plagioclases. Accessories are rich; the main role is played by amphiboles, epidote, and garnet (Table 1). The sandy material consists of slightly or completely unworked fragments (1-2-point rounding). Pelitic material is unevenly distributed. There is noticeably more of it in the dark-gray sediments. There, accumulations of pelite are mostly located in the space between grains; less often, clay minerals encase part of the terrigenous fragments with thin films composed of optically oriented crystalline aggregates. Clay material is represented by chlorite ($\approx 60-70\%$), mica (Fe-illite) ($\approx 25-30\%$), and smectite (5-10%). The clay material of marine Holocene deposits composing the bases of river terraces in the Olenitsa River valley has the same composition.

The light-brown color of the upper layer of sediment is due to the presence of a large amount of quartz and feldspar fragments of sandy and silty size, covered at the surface with a red-brown film of iron oxides. The amount of brightly colored grains does not exceed 25-30%. Grains covered with iron oxides are unevenly distributed in the sediment, sometimes concentrated in microlayers of like size. The jackets of iron oxides do not cement the sandy material. The dried sediment falls apart easily with pressure of the hand.

The underlying dark-gray sediment also contains grains colored red-brown with a film of iron oxides, but there are significantly fewer of them (no more than 10%). Analysis of the ratio of grains covered with a film of iron oxides and without it in the sediments under consideration leads us to believe that it is inherited or partially preserved on grains when material of the red-colored Terskii suite is destroyed and redeposited. In the layer of sediment with the dark-gray color, a significant part of the iron oxides brought in with terrigenous material was reduced. The large amount of hydrotroilite and pyrite can serve as evidence of this. The presence of hydrotroilite is connected with the dark-gray color of the sediment (in conditions of natural moisture content). When it dries out and oxidizes, it rapidly becomes light-gray. Pyrite, which forms isolated globules or composes irregularly shaped segregations consisting of accumulations of microglobules, is also a characteristic component of the association of secondary minerals in the dark-gray sediments. Pyrite is found particularly often in association with biotite, when microglobules of pyrite are located between the scales of swollen mica. Globular pyrite very often replaces plant remains. In the upper, light-brown layer of sediment, pyrite is rarely found.

The total content of organic-matter carbon in White Sea sediments is not high. The maximum enrichment with carbon ($C_{org} 2\%$) is noted in bays near the shore. The dark-gray sediments on the litoral at the mouth of the Olenitsa River contain significantly less carbon, which is concentrated mostly in the pelitic fraction (Table 2).

TABLE 1. Accessory Minerals of Marine Holocene Deposits of the White Sea

Contents in the 0.1-0.05 mm fraction, %	minerals															
	amphi- boles	pyrox- enes	musco- vite	bio- tite	epi- dote	tour- maline	sphene	zircon	garnat	dis- thene	silli- man- ite	stau- rolite	magne- tite	itmen- ite	pyrite	un- deter- mined
	48,5	8,3	0,6	0,9	15,3	—	2,8	0,3	14,1	0,6	0,6	0,3	0,6	7,1	—	—
	40,5	2,5	0,5	0,8	23,8	1,1	5,5	0,8	10,7	0,8	—	0,8	0,8	10,9	—	0,8
43,1	6,2	0,6	0,6	2,0	16,9	—	2,3	0,2	16,9	0,6	—	0,2	3,7	3,9	1,1	2,3

TABLE 2. Chemical Composition of Holocene and Pleistocene Marine Deposits

Dark-gray silt	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O ⁺	H ₂ O ⁻	CO ₂	C	Totals
1	67,27	0,64	13,62	2,19	1,63	0,04	2,60	2,93	3,82	2,44	0,11	1,51	1,14	—	—	99,94
2	49,93	1,13	16,78	6,60	2,14	0,11	4,62	2,06	4,33	3,15	2,06	7,32*	—	—	1,16	99,57
3	69,34	0,74	13,81	2,67	1,76	0,06	1,47	2,67	3,82	2,44	0,13	0,79	0,73	—	—	100,48
4	51,60	1,10	16,95	6,13	2,03	0,10	3,68	2,26	5,33	2,91	0,75	7,27*	—	—	0,63	100,74
5	58,84	0,96	14,66	3,83	2,09	0,06	3,60	2,10	2,03	2,87	0,13	3,02	3,77	1,02	0,79	99,95

Remark. *Total content of H₂O. 1-5) analyzed samples: 1, 2) deposits with gennoishas and concretions (1 – entire sediment, 2 – fraction <0.001); 3, 4) marine deposits in the base of the alluvial terrace (3 – entire sediment, 4 – fraction <0.001); 5) interglacial sediments, Varzuga River (entire sediment).

The taphacenos of these sediments includes a rich set of plankton and benthic organisms. Among the latter, O. M. Petrov identified *Mytilus edulis* (Linné), *Astarte (Trichula) borealis borealis* (Schumacher), and *Hiatella arctica* (Linné). Shells of these molluscs are found in single specimens or dense aggregations and, in many cases, are buried with two unseparated valves. Very many of them have a mother-of-pearl layer and organic matter of the upper, conchiolin layer. They all belong to subarctic, highly boreal forms and are present in the contemporary fauna of the White Sea.

Very thin and brittle aragonite (?) needles, solitary or collected in bundles, which are parts of destroyed *Mytilus* shells, are constantly present in the sandy-silty sediments. The very good preservation of individual needles may indicate a brief period and sparing conditions of redeposition of destroyed parts of the shells.

SHAPE OF CARBONATE FORMATIONS

Gennoishas. A rhombic, less often square bipyramid† is the main morphological element, various combinations of which determine the whole diversity of shapes of the gennoishas that are found. At the site studied, the main role is played by three morphological types of gennoishas, which are found equally often. The simplest in shape are bipyramidal gennoishas. These are distorted, broken (along the longitudinal axis) bipyramids, very elongated along the long axis, with sharp ends. Large specimens reach 20 cm along the long axis and 5 cm in the widest part, at the base of the pyramids. Bipyramidal gennoishas of considerably smaller size are also found, scarcely reaching 3 cm along the long axis. The ratio of the bipyramid's transverse dimension to its long axis varies from 1:6 to 1:2.

Multirayed (three, four, or more) intergrowths of rhombic and square bipyramids are joined in the second type of gennoishas, which are extremely diverse in the number, size, and interrelation of their rays. The dimensions of the rays in such intergrowths vary, but usually two-three rays have the greatest length (the maximum observed length is 5-6 cm), while the others are significantly smaller. In the areas where the rays adjoin, the shape of the pyramids is distorted. Large rays overgrow smaller ones, and the latter, as a result, often have an irregular, flattened shape. Large rays sometimes have a crooked, beak-shaped end of the pyramid.

The third morphological type of gennoishas combines spheroidal, sometimes somewhat flattened vertically, multirayed (ten or more rays) intergrowths in which the length of the greater part of the rays is similar. In shape, they are sometimes reminiscent of pineapples and reach a maximum of 6-7 cm across, but the greater part of them in the assembled collection is smaller (up to 3-4 cm in diameter). Smaller spheroidal concretions are also found, not exceeding 1-1.5 cm across. On cross sections of such gennoishas, one can see that they consist of a multitude of bipyramidal rays radiating from one center. Sometimes, the inner part of a bipyramid's ray is much shorter than the outer one, cramped by adjacent rays, and does not reach the central zone of the gennoisha. The inner parts of the bipyramids in such gennoishas are very distorted in shape (flattened, warped); some rays become trihedral in this area, and their ends do not touch, as a result of which crevices are formed in the central part of such gennoishas, spreading from the center in all directions.

The basic elements of sculpture of the rays' surface are the same for all of the morphological types of gennoishas. The difference is that on the surface of porous gennoishas the sculptural elements look coarse, sometimes with vague outlines. The surface of bipyramids and multirayed intergrowths combines sections of smooth faces consisting of a series of areas dropping off in ledges toward the base of the pyramid. The ledges are obliquely oriented (about 45°) in relation to the base (see Fig. 3a). Developed on two adjacent faces and coinciding at the edge, the ledges create a false pattern of coarse cleavage in the body of the pyramid. We should especially point out the presence of gennoishas in which the surface of the rays' faces is very uneven and bumpy; sometimes it is even somewhat concave, with sharply projecting uneven edges. In dense varieties of gennoishas, fine irregularities on the surface of the faces are leveled out by a thin layer of fibrous calcite, and they become smooth. The surface layer is formed by portions of fibrous calcite superimposed on each other (beginning from the edge, or the base of the pyramid), forming asymmetrical bumps, sometimes with sharp tips (see Fig. 3b-d).

†This definition of the shape is arbitrary to a significant extent, since warping of the faces and edges on a smooth or broken curve makes many gennoisha specimens not much resemble the crystals usually identified with a pyramidal shape.

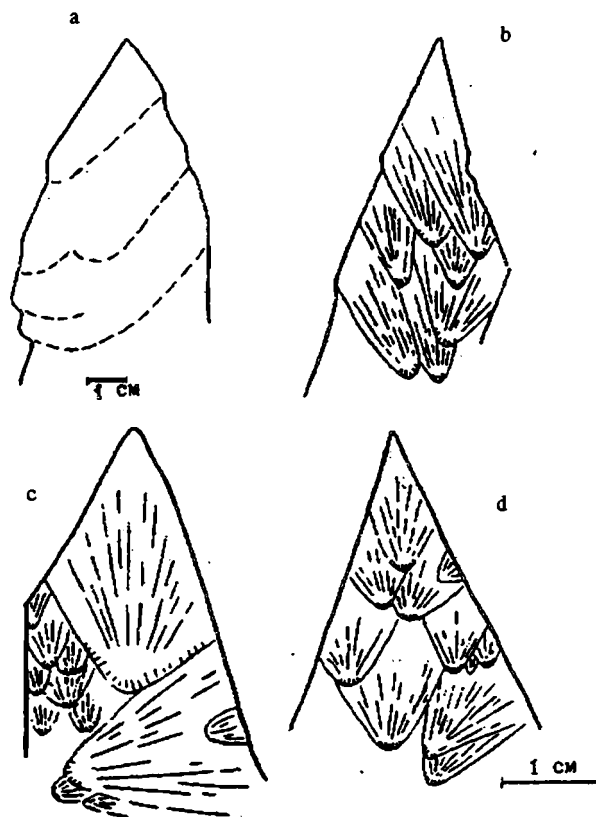


Fig. 3. Sculptural elements on the surface of gennoishas' rays (a – large sculptural elements creating a false pattern of the presence of coarse cleavage; b-d) fine sculptural elements composed of fibrous calcite).

Concretions. The whole diversity of collected concretion formations can be divided into four morphological types. The most widely developed are diverse tablets, often elongated in one direction. The ratio of thickness to length in them is from 1:10 to 1:20. The maximum observed length of concretions of this shape is about 20 cm. The surface of the tablets is uneven and gently bumpy; fine layering extending in conformity with the concretion's long axis and emphasized by the subparallel location of aggregations of plant detritus can sometimes be clearly seen on a fracture. Concretions of this shape often include numerous mollusc shells.

Spherical concretions with a flat, smooth surface are common at this site. The diameter of such concretions is from 2 to 8 cm. In the center of the greater part of spherical concretions are spheroidal gennoishas. Sometimes they are displaced to the edge of the concretion. The gennoishas' rays frequently project far out from the concretion.

Spindle-shaped concretions are usually formed around bipyramidal gennoishas, and also around bipyramidal gennoishas with small lateral outgrowths. The dimensions of this type of concretions are determined by the dimensions of the sealed-up gennoishas. The surface of the concretions is smooth, sometimes slightly wavy.

The fourth group of concretions is made up of isometric formations with rounded shapes, sometimes with a two-layer arrangement of thickenings. The size of such concretions reaches 20 cm along the long axis. They often include small spheroidal gennoishas and shells of marine molluscs, less often terrigenous fragments of gravel and pebble size. On their surface, concretions with an irregular shape often have complex relief formed by a combination of pits, bumps, or irregularly shaped swellings.

Finally, we should note the widespread phenomenon when gennoishas of different shapes are partially or completely covered by a jacket of sandy siltstone securely cemented by calcium carbonate.

It is important to emphasize that gennoishas sealed up are always significantly more dense, and on their surface under the concretion and on ends projecting out of it there is a "crust" formed by fine-fibrous (on a fracture) calcite.

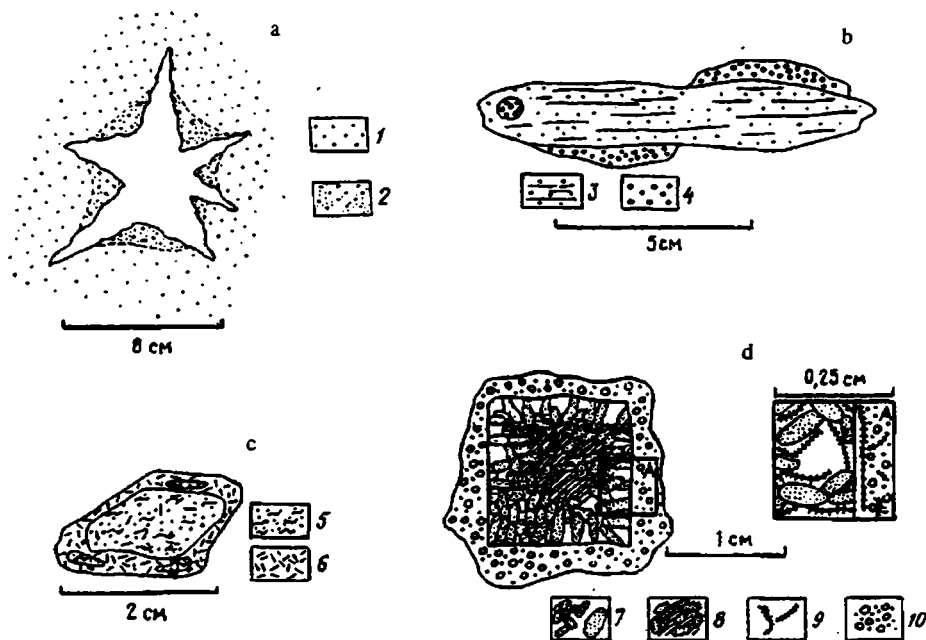


Fig. 4. Types of carbonate formations: a) multirayed gennoisha surrounded by carbonatized sediment of gelatinous consistency; b) concretion; c) cross section of "loose" bipyramidal gennoisha composed of terrigenous material in the central part; d) cross section of bipyramidal gennoisha sealed up in a concretion; 1) terrigenous noncarbonate sediment; 2) terrigenous sediment cemented with carbonate; 3) silty terrigenous material; 4) sandy terrigenous material; 5) dark-gray pelitic silt; 6) carbonate; 7) granular segregations of carbonate (see Fig. 5a); 8) poikilocrystalline structure; 9) filiform cryptocrystalline accumulations of calcite (see Fig. 5f); 10) terrigenous material cemented with carbonate of a concretion.

An interesting observation about the process of formation of concretions was made in studying gennoishas extracted from dark-gray silts. The gennoishas raised up from the bottom of the test pit (depth 0.5 m) were carefully packed together with the sediment surrounding them and sealed in a plastic packet on the spot. They were delivered to the laboratory in conditions of natural moisture content, where they were carefully freed from the surrounding sediment under a weak jet of water. In doing so, the loose sediment was easily washed away, and on the surface of the gennoishas, mainly at the base of the rays, a soft, gelatinous, gray-colored sediment was left (Fig. 4a). It was not removed from the surface of the gennoishas even under the action of a soft brush on it under a jet of water. The gelatinous sediment was easily pricked and destroyed with a needle. After three days of drying at room temperature, the sediment hardened and by then did not differ in strength from concretions collected on the surface of the tidal flat. Little pieces of hardened sediment placed in 2% HCl effervesce vigorously. In sections, the hardened sediment does not differ from carbonate concretions.

INTERRELATION OF CARBONATE FORMATIONS WITH SURROUNDING SEDIMENT

All of the concretions contain a large amount of terrigenous material. There is particularly much of it in tablet concretions. The sections in which replacement of terrigenous fragments by calcite was most strongly manifested have irregular, whimsical outlines in a cross section and are unevenly distributed in the body of the concretions, more often in the central part of them. On their periphery, tabletlike concretions just extracted from the sediment consist of weakly cemented terrigenous material easily destroyed by mechanical action. When they dry out, it hardens and does not differ in strength from the rest of the concretion. As a result, there are often "swellings" of securely cemented terrigenous material on the surface of the concretions. In a cross section of tabletlike concretions, thin horizontal layering is easily seen, sometimes disrupted as a result of the vital activity of limivorous worms (see Fig. 4b).

In spherical and complexly configured concretions, the microlayering of sediments is deformed and sharply broken off at the contact with the gennoishas sealed up in these concretions.

TABLE 3. Chemical Composition of Carbonate Formations, % (specimen 90/86)

Characteristics of the specimen	M.I.R.	R ₂ O ₃	CaO	MgO	CO ₂	C _{org}	Total	CaCO ₃	MgCO ₃	MgO _{sur}	CO ₂ sur
Gennoishas:											
porous	14,72	0,84	44,66	0,25	35,68	0,14	98,03	79,72	0,52	None	0,30
»	13,19	1,35	45,90	Her	36,00	None	96,44	81,70	Her	»	0,20
»	15,06	1,45	44,36	0,64	35,05	»	96,56	79,18	1,34	0,43	None
dense	1,92	0,68	49,66	3,07	41,35	»	96,68	88,64	6,42	0,58	»
»	3,75	0,59	49,46	2,57	41,40	»	97,77	88,29	5,37	0,22	»
»	21,60	1,32	38,00	2,77	32,70	»	97,78	67,83	5,50	0,14	»
»	13,41	1,54	41,94	3,21	36,25	0,54	96,89	74,65	6,72	None	0,04
»	11,11	1,49	44,07	2,20	37,10	0,22	96,19	78,44	4,61	»	0,32
Concretions:											
spherical	46,08	2,66	26,89	Her	21,55	0,64	98,23	48,00	None	None	0,42
»	47,92	2,65	23,83	1,99	20,25	None	96,64	42,54	4,16	0,58	None
»	45,19	3,40	25,17	1,62	20,85	»	96,18	44,93	3,39	0,62	»
irregularly shaped	40,90	0,82	27,33	2,09	23,10	»	94,24	48,64	4,37	0,45	»
tabletlike	46,54	4,17	21,61	3,03	19,90	0,70	95,95	38,46	6,33	0,23	»
	46,85	3,80	23,53	1,66	19,75	None	95,59	42,00	3,47	0,49	»

In the collection assembled there are gennoishas containing different amounts of terrigenous material (Table 3). There is very much sandy and silty material included in bipyramidal and multirayed porous gennoishas with coarse surface sculpture. Spheroidal porous gennoishas also sometimes contain loose sedimentary material inside the rays. In the upper, constantly washed layer of sediment it is easily removed, and one can often see gennoishas with a cavity in the central part of their rays. This phenomenon cannot be considered the result of selective destruction of carbonate material. Whole bipyramidal gennoishas are found in which only the outer part consists of pure carbonate, while the inner part is mostly dark-gray sediment with occasional grains of carbonate segregations (see Fig. 4c). Besides terrigenous material, fragments of mollusc shells, foraminifers, and cell walls of diatoms are found inside the rays.

As was noted above, on the surface of porous, coarsely sculptured gennoishas taken from the dark-gray sediment from a depth of 0.5 m we found clumps of silt saturated with gelatinous carbonate material that hardened upon drying. This material of a "future" concretion seals up the surface of unredeposited multirayed gennoishas with very elongated thin rays. On a transverse fracture, one can see the smooth interface of the gennoishas' surface and the sediment. Between the surfaces of the gennoishas' faces (uneven) and the sediment (smooth) are numerous empty cavities. A similar pattern is often seen at the contact of gennoishas and the concretions that seal them up. Inspection of a large number of fractures of concretions showed that the surface of the gennoishas sealed up in them is frequently also uneven and very porous, if the later concretion calcitization is "removed" (see Fig. 4d).

Gennoishas are very often found together with the shells of marine molluscs, with their rays frequently touching the shells. We were able to observe a multirayed gennoisha in which displaced fragments of one shell were clamped and partially enveloped. In another case, a large *Mytilus* shell was broken and pierced by a ray of a gennoisha in contact with it. This is a very important observation indicating the rays' gradual growth in length and width in sediment so dense that shells in contact with the growing rays of gennoishas could not be pushed aside.

The terrigenous components inside of gennoishas and carbonate concretions, and the surrounding sediment are similar in particle-size composition; their particles are mostly of silty size. In contrast to concretions and the surrounding sediment, gennoishas do not contain coarse-sandy or pebble material. The amount of terrigenous components in gennoishas varies in a wide range: from isolated grains to accumulations in which they amount to 10-15% or even more in specimens where the central part of the rays is composed of terrigenous material.

During the formation of gennoishas and concretions, mineral grains were fairly intensively dissolved. Regardless of their composition (quartz, potash feldspar, plagioclase, hornblende, etc.), mineral grains included in gennoishas and concretions are heavily corroded and replaced by calcite on their periphery. Frequently, only fragments of them remain, or they are completely replaced, and their former presence is guessed only from the shape of the carbonate pseudomorph.

MICROSTRUCTURE OF GENNOISHAS

On sections, the presence of no fewer than seven microstructural types of calcite segregations can be established in the structure of gennoishas of any morphological type.

First Type. The most common are formations reminiscent of rice grains or elongated granules (Fig. 5a). When they are magnified, one can see that these granules consist of individual fibers densely packed into bundles, sometimes with expanding or branching ends. In a cross section, the bundles are rounded or angular (tri- or tetrahedral), with a clearly manifested concentric structure. Sometimes, the bundles form cross-shaped intergrowths or have outgrowths. Terrigenous grains included in the outer part of the bundle are very seldom found. The maximum dimensions of calcite granules along their long axis are 0.4-0.5 mm. Inside of gennoishas, the granules are not oriented in any way, but chaotically distributed (see Fig. 4d). In the outer zone of the ray, they adjoin the inner surface at a tangent or form growths aimed into the ray obliquely or perpendicularly to its surface.

Second Type. Less often found are spheroidal segregations and diverse dumbbell-like intergrowths of them, sometimes crosswise intergrown, partially or completely fused spheres, etc. In a section of the spheres, the radial structure can be seen clearly, and the concentric structure less distinctly. The spheres are joined into dumbbells by fibers gathered into a bundle that smoothly turn into spheroidal structures. The maximum size of the spheres is 0.3 mm; and of the dumbbells, up to 0.5 mm along their long axis. Fragments of minerals are sometimes included in the outer part of the spheres (see Fig. 5b).

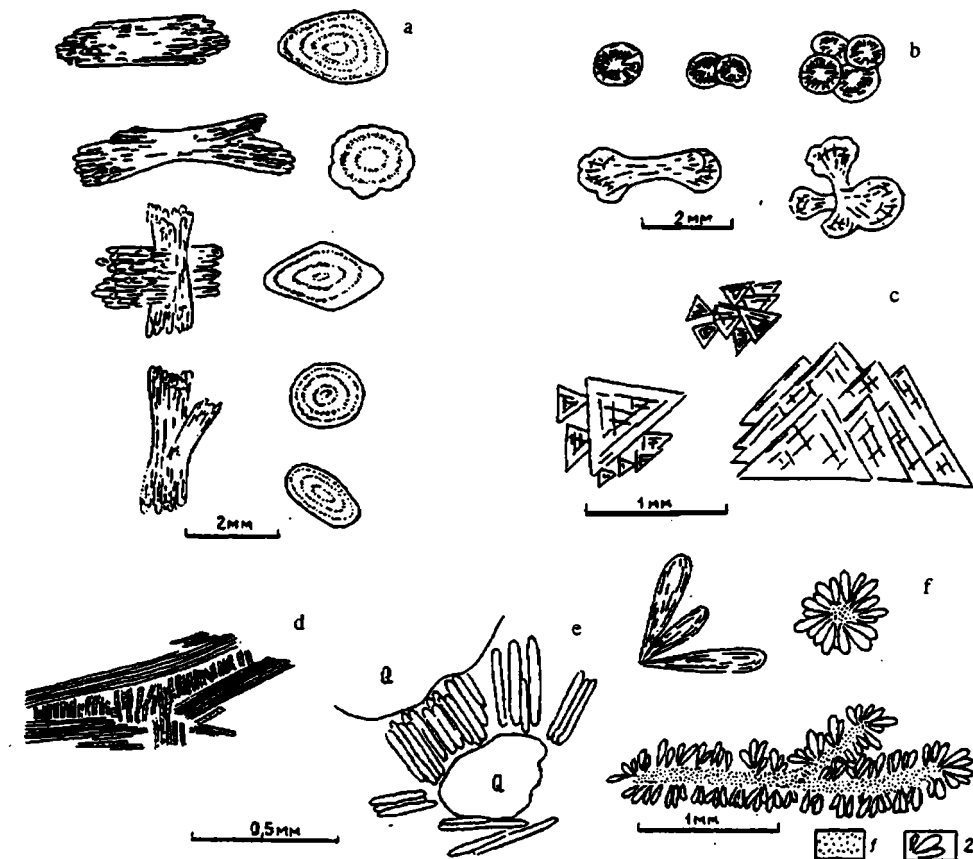


Fig. 5. Microstructural types of calcite segregations in the body of a gennoisha: a) granules, longitudinal and cross sections of calcite bundles; b) spheroidal segregations; c) pyramidal structures (triangles in the plane of the section); d, e) fibrous calcite segregations (d – between swollen biotite scales, e – between grains of quartz); f) calcite segregations; 1) cryptocrystalline accumulations; 2) brooms and fans composed of fine-fibrous calcite.

Third Type. Crystalline structures of various size. In the plane of the section they have the form of triangles; and three-dimensionally, of pyramids. They are occasionally found singly, more often in the form of diverse intergrowths (see Fig. 5c). These intergrowths sometimes form a framework consisting of various-sized pyramids oriented in space so that the faces of one pyramid are in contact with the vertices of adjacent ones.

Granules, spheroidal, and pyramidal structures are the main, and sometimes the only elements forming very porous gennoishas. They are irregularly distributed in the body of the gennoishas. For example, in some specimens an accumulation of spheroidal calcite segregations is noted in the outer part, while in others it is evenly distributed through the whole volume of the same type of gennoishas. Overgrowth of spheroidal structures by granules, in some cases, and partial inclusion of them in the body of the spheres, in others, allows us to think that they were formed simultaneously. Pyramidal structures are more often found on very porous sections of gennoishas. It should be emphasized that the three types of calcite segregations discussed are characteristic of gennoishas and are not found in concretions associated with them.

In the dark-gray sediment (in sections), occasional calcite segregations were observed that are formed by sub-parallel aggregates reminiscent of the bundles of fibers described above, composing granules. Such calcite segregations are found in a fine-grained matrix between scales of swollen biotite particles and sandy grains of quartz (see Fig. 5d and e).

In dense gennoishas, and also in very porous ones around which a concretion has already formed, cryptocrystalline and fine-fibrous calcite segregations forming the following morphological types are widespread.

Fourth Type. Cryptocrystalline accumulations of calcite composing jackets around earlier carbonate structures and terrigenous fragments, and also filiform formations lying on the surface of granules and spheres, and suspended in the pore space between them.

Fifth Type. On the surface of granules and spheres, and also of cryptocrystalline calcite segregations, are fine-fibrous formations reminiscent in shape of a fan or broom, narrowing sharply toward the base and rounded off in the outer part (see Fig. 5a). Appearing in mass, they form crustification fringes; and in pore space, chaotically located, sometimes cross-shaped intergrowths.

Sixth Type. The densest gennoishas and some concretions have a poikilocrystalline structure. In this case, large crystals of water-transparent calcite include all or part of earlier carbonate formations. More often, this phenomenon is observed in the central part of the rays of gennoishas and concretions; sometimes it encompasses them entirely. The fifth and sixth types of calcite segregations are also characteristic of concretions.

Seventh Type. A special position is occupied by the structure of the outer jacket of gennoishas (see Fig. 3). This is a structural type of calcite segregation which, when fully developed, gives gennoishas a smooth, fine-bumpy surface. In the assembled collection, this structural type of calcite segregation is seldom found, only on certain specimens, regardless of the gennoishas' morphological peculiarities. Small bumps with a smooth surface and sometimes with a silky luster are composed of fine fibers oriented radially from the top of the bump. Usually, this is a series of unequal-sided bumps joined together, which have the steep slope oriented toward the base of the pyramid on the faces of a ray, and toward the central axis of the gennoisha's ray near the edges. Sometimes, the bumps are located one by one or several at once in a chain, extending along the ray's long axis. The chain of bumps can also be located across the long axis, but this is found, as a rule, in the middle part of bipyramidal gennoishas. The successive formation of individual portions of the outer jacket is emphasized by partial overlapping of the bases of adjacent bumps, which are arranged so that the latest formations are at the ends of the rays. That the outer jacket was formed last is emphasized not only by its position on the surface of the gennoishas, but also by the indicated peculiarities of its structure.

Summarizing peculiarities of the morphology of gennoishas and their internal structure, it is not hard to see that the rays lengthened and expanded in the process of formation, and carbonate material gradually replaced the surrounding terrigenous sediment.

CHEMICAL AND ISOTOPIC COMPOSITION OF GENNOISHAS AND CONCRETIONS

The contents of mineral insoluble residue (M.I.R.) in most gennoishas is significantly less than in concretions (see Table 3). This agrees well with the high rate of replacement of mineral grains by carbonate in them, which was noted above. It is important to emphasize that porous and dense gennoishas practically do not differ in their contents of mineral insoluble residue, although among the latter examples are found with very small content of insoluble mineral components. Consequently, the greater part of the terrigenous material was dissolved in an early stage of formation of the gennoishas' internal structure, during formation of the first two microstructural types of segregations of calcium carbonate (granules and spheroidal segregations).

According to x-ray data (Fig. 6), the main component of gennoishas is CaCO_3 . Chemical investigation showed that the average content of CaCO_3 is approximately the same in porous and dense gennoishas. In concretions, the main neogenic component is also CaCO_3 . Porous gennoishas contain very little MgO or none at all. A significant increase in this element is noted in dense gennoishas and concretions, although among the latter purely calcite ones are found. From the data obtained (Table 3), we can see that gennoishas and concretions at the site under investigation are mostly composed of calcite, sometimes with a significant admixture of low-magnesian calcite. Such a composition is characteristic of gennoishas of a wide age interval: from the Permian to the Pleistocene from various sites in the Northern and Southern hemispheres [4]. Comparison of the results of petrographic and chemical investigations of White Sea gennoishas allows us to come to the conclusion that the earliest structural elements of their internal structure mostly consist of calcite, while low-magnesian calcite takes a noticeable part in the structure of later ones and concretions.

To determine the concentration of ^{14}C , from the upper horizon of dark-gray sediments (see Fig. 1) we took three specimens of gennoishas differing in density. The measurements were made on a two-channel scintillation β -spectrometer. Specimen 90/86a is a dense, bipyramidal gennoisha; specimen 90/86b, a multirayed gennoisha with unevenly distributed porosity and poikilocrystalline CaCO_3 in the central part of the ray; specimen 90/86c, a flimsy spheroidal gennoisha easily broken by hand. The following ages were determined for the gennoishas, 1000 years: specimen 90/86a — $10,140 \pm 150$

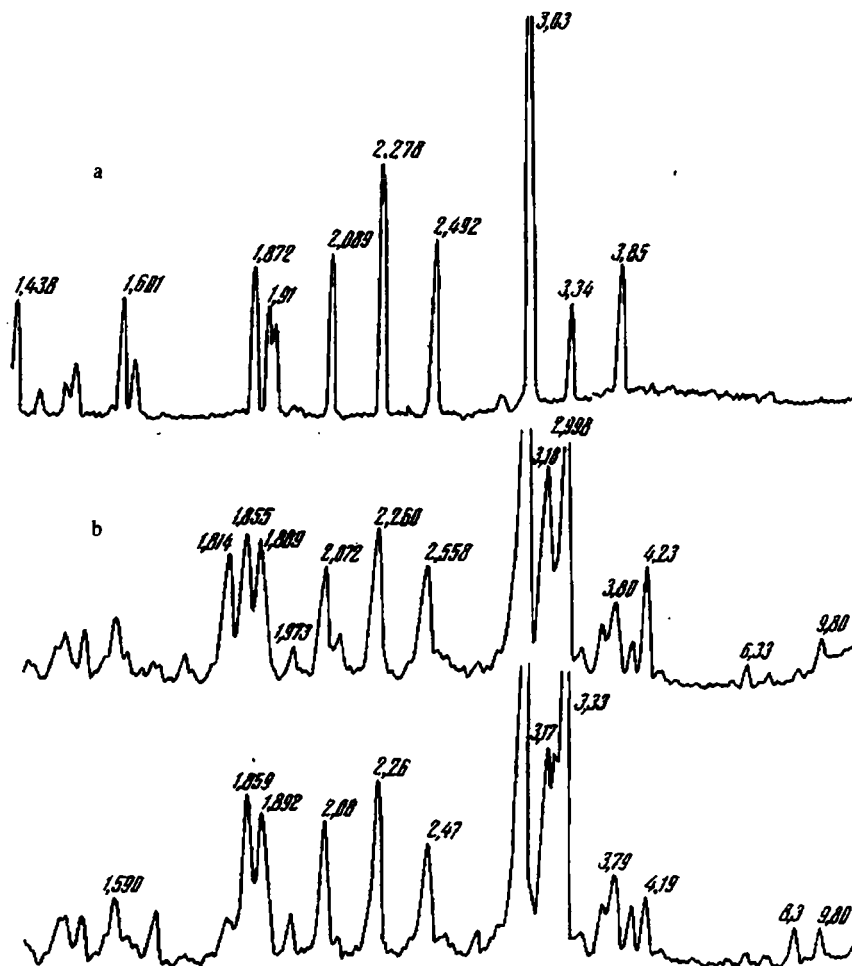


Fig. 6. Diffractograms of powder preparations of gennoishas (a) and concretions (b); specimen 90/86.

(GIN 6611), specimen 90/86b - 9440 ± 186 (GIN 6612), and specimen 90/86c - 9630 ± 250 (GIN 6613). At present, it is hard to unequivocally evaluate the reliability of these data. Additional collections of organic material need to be made in the sediments surrounding gennoishas, and the composition of these sediments' gas phase should also be analyzed.

Based on the conditions of the gennoishas' occurrence (see Figs. 1 and 2) and the widespread extent of marine Holocene deposits in this region, we can say with high probability that formation of White Sea carbonate neogeneses began in the Holocene. It cannot be ruled out that the dates obtained should be somewhat older. If the gennoishas' carbonates are a biogeochemical formation, this phenomenon could be connected with the use of carbon in methane penetrating (rising up) into Holocene sediments from older deposits underlying the moraine. It is interesting to pay attention to the close age values for gennoishas of varying density. Even if they do not correspond to the actual time of formation, they do indicate close concentrations of ^{14}C in gennoishas with varying density and contents of terrigenous material. And this may be interesting, in turn, as a certain indication of simultaneous, but nonuniform development of the internal structure of various gennoishas.

To investigate the isotopic composition of carbon and oxygen also from the upper horizon of dark-gray sediments (see Fig. 1, specimen 90/86), we took: a porous spheroidal gennoisha, dense spheroidal and bipyramidal gennoishas, a spherical concretion formed around a gennoisha, a tablet concretion with numerous remains of sea shells, and shells of marine molluscs extracted from a tablet concretion (see Table 2). For isotopic analyses of carbon and oxygen, the samples were decomposed with the help of H_3PO_4 . The isotopic composition was determined on an MI-1201 V mass spectrometer. The values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are given pro mille in relation to the PDB standard. The error in determining $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ does not exceed $\pm 0.2\%$.

As we can see from the data obtained (Table 4), the isotopic composition of the carbon and oxygen in gennoishas and concretions is similar. The carbonate in different types of gennoishas and in concretions is characterized by slight (from -14.0 to -22.4) variations in the values of $\delta^{13}\text{C}$. The lowest value of $\delta^{13}\text{C}$ was found in a dense pyramidal gennoisha. Practically all of the carbon in it was taken from organic matter. The somewhat heavier relative isotopic composition of carbonate in a tabletlike concretion with numerous remains of marine mollusc shells is apparently connected with contamination of the sample by the sea shells' material ($\delta^{13}\text{C} = -2.0$).

The isotopic composition of oxygen varies in a narrow range (from -2.9 to -0.4). The values of $\delta^{18}\text{O}$ in gennoishas and concretions are practically identical to the values of $\delta^{18}\text{O}$ in marine mollusc shells (-2.4) and are near the limits of the "normal marine" interval.

According to the values of $\delta^{13}\text{C}$ and $\delta^{18}\text{C}$, White Sea carbonate neogeneses differ little from contemporary formations of hexahydrate calcium carbonate from the Antarctic shelf that are morphologically similar to bipyramidal gennoishas (see Table 4) [17].

Gennoishas and concretions with isotopically light carbon are also found in Pleistocene deposits of Taimyr (see Table 4), in Tertiary deposits of Western and Eastern Kamchatka,** in Tertiary deposits of America [11], and in Cretaceous deposits of Canada [16]. However, in Tertiary and older deposits, as a result of superimposed processes of change, the gennoishas (and concretions paragenetically associated with them) can have higher values of $\delta^{13}\text{C}$, due to contamination of the samples with later, catagenetic [late diagenetic] calcite. Therefore, the White Sea gennoishas and concretions, which are unaffected by secondary transformations, give a very good example of diagenetic carbonate neogeneses, the isotopic composition of C and O in which has remained unchanged. The isotopic temperatures calculated for these carbonate neogeneses may be closer to the true ones.

It is known that surface waters of the Arctic basin are 4‰ poorer in $\delta^{13}\text{C}$ than the usual seawater [2]. The values of $\delta^{18}\text{O}$ for White Sea waters at the time of the gennoishas' formation are unknown, but apparently they were fairly close to the contemporary values. In the White Sea, the average values of $\delta^{18}\text{O}$ for surface waters (down to depths of 10-15 m) are characterized by values from -3 to -6 ‰; and of deep waters, from -1.5 to -3.0 ‰ [8]. In estimating variations in the isotopic composition of oxygen during the Holocene, we have to take into account that in shallows the waters of the White Sea may have been significantly fresher than at present.

The isotopic temperatures, calculated according to the formula [14] $T = 16.5 - 4.3(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.14(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2$, where $\delta^{18}\text{O}_c$ is measured values of $\delta^{18}\text{O}$ in carbonate in relation to the PDB standard, and $\delta^{18}\text{O}_w$ is the isotopic composition of water in relation to the SMOW standard, fall in the interval of 2.8 - 11.9°C (see Table 4). It may be that the temperature of formation of White Sea carbonates was somewhat overstated, due to failure to consider the stronger freshening of waters of the White Sea. According to the value of the Z criterion (considerably less than 120), White Sea gennoishas and concretions should be classified as freshwater limestones [15].

DISCUSSION OF RESULTS AND BASIC CONCLUSIONS

The available data lead us to believe that the deposits in which gennoishas are embedded were formed after the accumulation of glacial and marine clays that were deposited from the early Dryas all the way up to the pre-Boreal [3, 7]. In the stable conditions of subglacial sedimentation, the moraine sheet was not disturbed, and fine-grained silts accumulated, which are practically devoid of remains of marine fauna. After destruction of the glacial armor at the beginning of the Boreal, subglacial accumulation of fine-grained sediments was replaced by hydrodynamically more active marine conditions. At that time, erosion of the moraine began on slightly raised sections of the bottom. Comparison of the deposits of late-glacial and postglacial marine basins in the southern part of the Kola peninsula makes it possible to determine the beginning of formation of strata of Holocene sediments composing the base of the terraces approximately at the turn of 10,000-9000 years [5]. This agrees with the datings of gennoishas given above.

**These data are being prepared for publication.

TABLE 4. Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in Carbonate Neogeneses and Marine Mollusc Shell

Indices	Holocene deposits, White Sea						Contemporary sediments of the Antarctic shelf (ikaite)	Pleistocene deposits, Taimyr			
	gennoisha			concretion		marine mollusc shell		gennoisha			concre- tion seal- ing up a gennoisha
	spheroi- dal dense	spheroidal porous	bipyra- midal	tablet- like	spheroidal around a gennoisha			sphe- roi- dal	spheroi- dal	spheroi- dal, sealed up in a concretion	
$\delta^{13}\text{C}$ (PDB)	—16,1	—17,0	—22,4	—14,0	—16,3	—2,0	—22,88 + + —18,79	—4,5	—5,4	—21,4	—15,1
$\delta^{18}\text{O}$ (PDB)	—0,6	—2,9	—2,3	—0,4	—0,5	—2,4	3,3 + + —3,8	—3,6	—3,6	—1,7	—2,6
$T, ^\circ\text{C}^{**}$	3,5	11,9	9,6	2,8	3,2	9,9	—	14,8	14,8	7,3	10,8

*According to [17].

**Temperatures calculated for $\delta^{18}\text{O}$ of water equal to -4.0.

In the process of preparation and discussion of this work, Yu. A. Lavrushin and A. G. Chernyakhovskii expressed a hypothesis about a connection between the formation of local carbonatization and inflow of hydrocarbons from deeper layers of the Earth's crust. In fact, the rupture dislocation that passes precisely through this region may have served as a conducting channel for carbon-containing gases and resulted in the local nature of appearance of carbonate mineralization in Holocene sediments.

The light composition of carbon isotopes provides a basis for thinking that the carbonate in gennoishas and concretions was formed by carbon dioxide resulting from microbiological decomposition of organic matter. At the same time, the sediments in which gennoishas are embedded contain a very small amount of organic carbon, while glacial and marine deposits formed mostly on account of glacial material are also extremely poor in organic matter. We will recall that gennoishas and concretions are found locally, at the site of an eroded moraine sheet. This allows us to suppose that under the moraine in this region deposits rich in organic material were preserved from abrasion. For example, these could be interglacial marine deposits (see Table 2) analogous to those exposed in the adjacent region, in the Varzuga River valley. According to available seismoacoustic data, on the greater part of the bottom of the White Sea, Vendian and Riphean deposits, which may also contain gaseous hydrocarbons, are located directly under the moraine [9]. The moraine sheet served as a screen preventing removal of gaseous products of the decomposition of organic matter from the sediments underlying it. Perhaps, under the layer of ice and moraine there was a zone of hydrate formation, which resulted in accumulation of hydrocarbons [10]. Abrasion of the moraine sheet on the elevated section of the bottom opened up the possibility of migration of accumulated gases upward, into marine sediments overlying the moraine.

The organogenic nature of gennoishas was first suggested by N. G. Brodskaya and N. V. Rentgarten [1], based on peculiarities of the internal structure of gennoishas that, in their opinion, are similar to fossilized remains of algae (Rhodophyta). At present, it is hard to agree with this. Existing data show that the formation of gennoishas occurred in sediment at a certain depth in a reducing situation, which completely rules out the development of algae.

The most important condition for formation of a precursor of gennoishas, ikaite, is believed to be the presence in the sediment of low, close to zero, or even negative temperatures, and high hydrostatic pressure (~ 6 kbar) [17]. Now we know that gennoishas may also have formed in shallow-water, sublittoral conditions. The necessary situation for formation may have been created in the sediment against a background of low temperatures locally as a result of bacterial metabolism.

The carbonate's bacterial origin is confirmed by the morphological diversity of microstructural types of calcite segregations and the similarity of some of them with carbonate formations of clearly microbiological origin [12].

The concept of microbial origin of gennoishas makes it possible to suggest an explanation for certain peculiarities of their structure and conditions of their formation. Formation of the precursor mineral (ikaite) occurred in strata of sediment in early stages of diagenesis. Formation of ikaite, its replacement by calcite, and an increase in the number and size of the rays occurred discretely. This process can be represented in a general form as follows. The ikaite crystals that had formed included a large amount of terrigenous material. Especially favorable conditions for intensive bacterial activity and destruction of silicate material arose inside the ikaite crystals. Gradually, beginning from the crystal's walls, the ikaite was replaced by granular and other types of calcite segregations. Replacement of each forming portion of the precursor mineral by calcite occurred practically without a change in volume. Since the destruction of ikaite and formation of CaCO_3 are accompanied by an almost 20-fold decrease in volume [17], for inheritance of the crystallike shape one has to assume fairly rapid formation of the diverse types of calcite segregations noted above. New portions of ikaite already formed on the surface of rays consisting of calcite. This was repeated many times. More often, the ikaite formed at the ends of the rays, but it may have appeared simultaneously on their faces as well. As a result, the rays lengthened and grew in width, or outgrowths formed, sometimes so numerous that spheroidal gennoishas were gradually created.

The fact that gennoishas and concretions are found together, the similarity of certain microstructural types of calcite segregations, and the close chemical and isotopic composition of carbon lead us to believe that the concretions also formed as a result of vigorous bacterial activity.

The presence of carbonate sediment of gelatinous consistency (fixed by carbonate material) on the surface of some gennoishas indicates that the process of carbonatization is continuing even now. Study of this process and clarification of the reasons for its local extent are the tasks of future investigations requiring a comprehensive geological, geochemical, and microbiological approach.

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Fe AND Mg IN OCEANIC CONCRETION ORES. SEDIMENT GENESIS AND THERMAL SAMPLE TREATMENT

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The various types of oceanic Fe–Mn concretions samples were air-heated to maximum 1000°C. As a result, mineral phases in complex hydrogenic-depositional, diagenetic-sedimentary and the Halbach "early diagenetic" stages were transformed essentially into Mn-spinel. X-ray diffraction patterns indicate that diagenetic Fe–Mn concretions after heating consist of two, hausmannite and Mn-spinel phases. This indicates their complex primary composition and structure.

Birnessite minerals of sedimentary and hydrothermal origins, present in Pacific Ocean microconcretions as well as lenses and layers in Okhotsk Sea tephroid sandstones have been progressively heated to 200, 400, 600, 800, and 1000°C temperatures. Products of these experiments were studied by x-ray phase analysis [20].

Hydrothermal birnessite between 400–600°C transformed into tetragonal hausmannite, Mn_3O_4 . During subsequent heating to 800°C then to 1000°C hausmannite reflections became gradually sharper, indicating improved crystal structure ordering.

Another alteration trend involved sedimentary birnessite. Between 400–600°C hausmannite and Mn-spinel (Mn_3O_4) phases appeared in the diffraction pattern. In contrast to hausmannite, Mn-spinel belongs to the cubic crystal system. As the diffraction patterns show, further heating markedly lowers the hausmannite peak height. That peak disappears altogether at 1000°C while the spinel peak increases significantly.

The contrasting behavior of sedimentary and hydrothermal birnessites during heat treatment is due to the fact that sedimentary birnessite that includes Cu and numerous other elements is less stable than its hydrothermal variety and contains practically none of these elements. The great stability of hydrothermal birnessite, heated in air at high (maximum 1000°C) temperatures, in contrast with its sedimentary variety) suggested [20] this feature as a diagnostic indicator in a genetic system [22] that includes sedimentary and hydrothermal oceanic mineral matter.

In contrast with a previous publication [20] the present paper contrasts the thermal behavior of various oceanic Fe–Mn mineral substances. Sedimentary, sedimentary-diagenetic, and diagenetic genetic categories have been identified. Our objective was to establish differences within the genetic system. The mode of Mn-phase transformation during high-temperature heating was of prime interest. Changes are closely associated with minor and trace elements, major components in the Mn-concretions. To a much lesser degree, the elements also occur in the iron phase.

BASIC CATEGORIES OF SEDIMENTARY OCEANIC Fe–Mn CONCRETION ORES

The large recent literature on classification problems of Fe–Mn concretion ore include very useful [5] recommendations [22]. Halbach and others [23–27] recommended a separate system.

Bonatti and others [22] grouped oceanic Fe–Mn concretions as follows:

(1) Hydrogenic (sedimentary) concretions, formed during slow deposition of ore and other elements from sea water. The process of hydrogenic concretion and crust formation takes place in oceanic abyssal plains, with simultaneous development of dispersed microparticles and microconcretions. Hydrogenic substances have 0.5–5.0 Mn/Fe ratios and high concentrations of minor elements, as Ni, Cu, and Co.

(2) Diagenetic concretions of hemipelagic ocean margin zones. They are essentially Mn-concretions of very small iron content, with practically no trace elements. This composition was due to postdepositional remobilization of Mn and a series of other metals in sediments, enriched in organic matter.

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TABLE 1. Element Composition in Studied Fe – Mn-Rich Substances Middle, and Inner Concretion Portions, Respectively

Sample number (station)	Type of substance	Sample location	Genetic type of substance	Coordinates and depth, in m	Content, in %					Mn/Fe
					Mn	Fe	Ni	Cu	Co	
611	Concretions	Pacific Ocean, deep oceanic Marcus-Necker Rise	Sedimentary (hydrothermal) (B)	17°29' N. lat. 171°30' E. long. (4190)	14,72	16,74	0,280	0,140	0,310	0,88
675	*	Pacific Ocean, NE part of Clarion Fracture Zone	Sedimentary (diagenetic) (AB)	19°02' N. lat. 116°22' E. long. (3910)	26,12	8,41	1,200	0,860	0,130	3,10
2483-12	*	Pacific Ocean, NE part of Clarion-Clipperton Fracture Zones	Sedimentary, diagenetic (A)	10°02' N. lat. 146°24' E. long. (5074)	26,30 26,60 25,20	5,80 5,60 3,60	1,000 1,200 1,340	0,760 1,050 1,020	0,300 0,190 0,150	4,53 * 4,75 ** 7,00 ***
82105	Cylindrical concretions	Pacific Ocean, ocean floor slope of Central American Trench	Sedimentary, diagenetic	18°08' N. lat. 104°43' E. long. (4060)	56,80	0,30	0,008	0,010	0,002	196
7783	Crusts	Sea of Japan, north slope of nameless seamount	Hydrothermal	39°55' N. lat. 136°40' E. long. (1600)	46,60	0,050	0,006	0,004	0,005	930

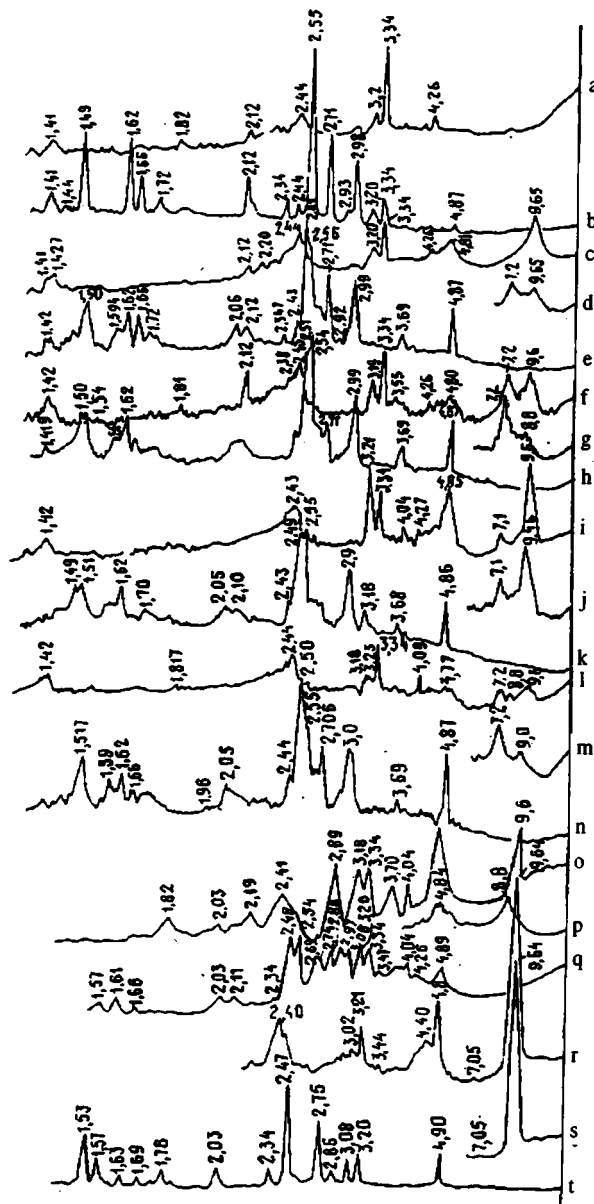


Fig. 1. X-ray diffraction curves from original and heated Fe-Mn concretions and crusts.

δMnO_2 and 10 Å-manganite are the main minerals of oceanic Fe-Mn concretions and crusts, formed by hydrogenic and diagenetic means [22]. In contrast with hydrogenic Fe-Mn crusts and diagenetic concretions, Ni and other trace elements are almost completely absent from diagenetic and hydrothermal crusts and concretions.

(3) Halmyrolytic formation related to atmospheric oxygen-enriched sea water impact on basaltic volcanic glass. Fe and Mn-hydroxides, Fe-smectite, and the zeolite phillipsite were end products of this process.

Study results of Fe-Mn concretions and crusts from the northeastern Pacific Clarion-Clipperton fracture zone and the east Pacific Peru Basin led to the new classification of Halbach and coauthors of oceanic Fe-Mn sedimentary mineralizations. Two types were recognized:

(A) an early diagenetic type, associated with metals in pore water, derived from the top, active, 5-30 cm thick, semiliquid layer; and

TABLE 2. Reflection Intensities (I) and Interlayer Distances (d) from X-Ray Patterns of Mn, Fe-Mn, and Fe-Minerals [8]

Hausmannite Mn ₃ O ₄ (1—1127)		Mn-oxide (spinel) Mn ₃ O ₄ (13—162)		Bixbyite (Mn, Fe) ₂ O ₃ (8—10)		Jacobsite MnFe ₂ O ₄ (10—319)		Goethite α -Fe ₂ O ₃ ·H ₂ O (8—97)		Hematite α -Fe ₂ O ₃ (15—534)	
I	d	I	d	I	d	I	d	I	d	I	d
—	—	—	—	—	—	—	—	20	5,000	—	—
20	4,92	—	—	—	—	40	4,94	—	—	—	—
—	—	50	4,86	—	—	—	—	—	—	—	—
—	—	—	—	10	4,68	—	—	—	—	—	—
—	—	—	—	10	4,21	—	—	100	4,210	—	—
—	—	—	—	60	3,83	—	—	—	—	25	3,660
—	—	—	—	10	3,35	—	—	20	3,370	—	—
31	3,08	—	—	—	—	—	—	—	—	—	—
—	—	50	2,98	30	2,99	40	3,01	—	—	—	—
8	2,87	—	—	—	—	—	—	—	—	—	—
63	2,75	—	—	100	2,72	—	—	8	2,690	100	2,690
—	—	—	—	—	—	—	—	20	2,570	—	—
—	—	100	2,54	20	2,51	100	2,56	10	2,510	50	2,510
100	2,48	10	2,43	—	—	3	2,45	20	2,480	—	—
13	2,36	—	—	40	2,35	—	—	70	2,44	—	—
—	—	—	—	20	2,21	—	—	20	2,250	—	—
—	—	50	2,10	10	2,11	40	2,12	40	2,180	—	—
15	2,03	—	—	40	2,01	—	—	10	2,000	30	2,010
—	—	—	—	10	1,92	—	—	—	—	—	—
—	—	—	—	40	1,87	—	—	—	—	—	—
18	1,79	—	—	—	—	—	—	—	—	40	1,831
5	1,70	20	1,71	25	1,72	10	1,73	50	1,719	—	—
5	1,64	—	—	90	1,65	40	1,64	20	1,684	60	1,690
—	—	50	1,62	20	1,61	—	—	—	—	—	—
50	1,57	—	—	20	1,56	—	—	—	—	16	1,594
50	1,50	50	1,49	30	1,53	60	1,50	—	—	—	—
3	1,47	—	—	20	1,48	—	—	—	—	35	1,480
8	1,44	—	—	30	1,45	5	1,43	—	—	35	1,450
—	—	—	—	80	1,42	—	—	—	—	—	—

(B) a hydrogenic (sedimentary) type. Metals for concretion ore development came from the ocean bottom water layer. These processes controlled formation of various Fe-Mn concretions; the A-early diagenetic; B-hydrogenic (sedimentary); the AB-mixed type (upper unit; metals derived from ocean bottom waters, the lower unit metals from the pore waters). The Ac category was also genetic, typical of the Peru Basin.

The concretion ore types may be easy to identify [23-27] by the nature of the upper boundary of the concretions, the ore fraction mineralogy, as well as the interior microstructure and geochemistry. Halbach and coauthors indicated that the Mn/Fe ratios represent key indicators of concretion ores with the following values: hydrogenic: low (<2.5) ratios; mixed sedimentary-diagenetic: 2.5-4; diagenetic A category: high (>4-5) ratios, category Ac: very high, >6-7 ratios, with minor amounts of Ni, Cu, and several other trace elements.

δ -MnO₂ was the dominant mineral of hydrogenic concretions. It was closely associated with Fe(OOH) and Al-silicates. Todorokite (10 Å-magnetite) was the main mineral of diagenetic (A and Ac) concretions in the Peru Basin. When heated for 2 h at 105°C, it turned into birnessite. This indicated [23-27] that todorokite does not have a tunnel-type but a layered structure in the diagenetic Ac-concretion category.

Academician Chukhrov and coauthors at IGEM and GIN, Russian Academy of Sciences, have reviewed the mineralogy of oceanic Fe-Mn substances and established the presence of previously unknown Mn and Fe-phases in these materials [17, 18].

Skornyakova, Uspenskaya and others [11-13] utilized data [17, 18, etc.] in the study of the mineralogy of the hydrogenic (B), mixed (AB), and diagenetic (A and Ac) types of sedimentary ocean concretions from the Pacific. This supplements their macro- and microscopic descriptions, chemical and other analyses that identified compositional, structural and area distribution characteristics of these substances.

SAMPLES AND STUDY METHODS

Various Fe–Mn concretion ores, taken from the Pacific Ocean floor have been studied (Table 1). According to the literature they are of sedimentary (hydrogenic), sedimentary-diagenetic, diagenetic [23-27] (types A or Ac), and of diagenetic origin.

A publication [20] discussed subsequent gradual heating of sedimentary and hydrothermal birnessites to 200°C and higher. It included associated x-ray diffraction analysis results. In contrast, we heated samples at 105°C for 2 h, and then bypassing intermediate phases, to 1000°C. This was done by thermograph, brand name "Derivatograph," Q = 1000, produced in Hungary. The mineral composition of the heating products at 105° and 1000°C was determined by x-ray phase analysis. We believe that when the intermediate heating products are disregarded in a study the initial phase reduces the time required for the experimental procedure. This did not compromise the study results.

The study of various heated Fe–Mn ocean sample types requires a very careful analysis of the initial mineral phases. Samples taken during the 9th Cruise of R/V *Dmitrii Mendeleev*, the 8th Cruise of R/V *Academician Nikolai Strakhov*, and also obtained from N. S. Skornyakova, Oceanology Institute, RAS, were studied by very similar methods. These included macro- and microscopic, x-ray diffraction, chemical, spectral and other analyses. Microdiffraction analysis played a main role. It was conducted under the supervision of Prof. A. I. Gorshkov, (IGEM, Russian Academy of Sciences).

In addition to sediments, taken in various Pacific areas, for comparison purposes Sea of Japan todorokite samples were received A. N. Dergachev (TOI, DVNTs). The basic sample analysis data is summarized in Table 1.

BRIEF DESCRIPTION OF ANALYZED SAMPLES AND HEATING RESULTS

(A) Station 611 (9th Cruise of R/V *Dmitrii Mendeleev*) is located in the Marcus-Necker seamount zone. The pelagic sediments in the area consist of clayey muds, with inclusions of carbonate mud and coarse detrital matter. The lower sediment section often consists exclusively of carbonate deposits [6].

Sediment accumulation and formation of Fe–Mn concretions occur in the oxidized [10, etc.] in the total absence of reducing processes ($E_h = +550; +600$ mV. The organic matter content was small (0.15-0.24%). Fe content: 3.78%, Mn = 0.39% [2, 3]. According to Pushkina [9] who studied muddy pore waters that were squeezed out of sediments near Station 612, also in the Marcus-Necker seamount region (17°57'N, 177°39'E, 4470 m), the Mn content in the top sediment layers (0-5 cm) was 40 μg [1], the Fe content, 20 $\mu\text{g/liter}$.

Lower abundance (0.5 kg/m²) marks concretions from Stations 611 and 612. They are somewhat elongated, oval, and small (10-15 mm long, 5-6 mm wide). The surfaces are usually smooth, fine-grained. Certain amount of roughness dominates in given surface areas. Microscope studies indicated the presence of two, structurally sharply separated zones, an interior and an exterior zone. The surface layer is very thin (0.4-0.5 mm), dominated by columnar structures, and is composed of Fe and Mn-hydroxides, as well as fine biogenic-terrigenous matter. Globular features occur in the direction toward the concretion interior. The concretion interiors at Station 611 consist of collomorph, globular and columnar structures. Massive structures occur occasionally in these concretion parts. The concretion center includes small palagonitized basalt fragments, characterized by uneven-angular shapes; indications of their nearby source matter.

Certain portions of the concretions include fracture of various orientation. These cut through interior and exterior concretion areas. As a rule, they are filled by younger Fe- and Mn-hydroxide generations. Thin lenses and laminae of relatively highly reflective matter occur among the collomorph and columnar features. This matter is anisotropic and observable under microscope with crossed nicols. Microprobe studies (Kameka, MS-46), conducted on a number of such interior and exterior portions of concretions indicated high Mn/Fe ratios (3-4, occasionally 5). The chemical analysis of concretions indicated that the basic chemical element content, Mn and Fe, is small (Table 1). It clearly differs from similar substances in the more oxidized zone of the Pacific Ocean, eastward across the profile.

Concretions of Station 611 are characterized by clearly reduced Mn/Fe ratios. They include somewhat increased Ni, Cu, and Co concentrations (Table 1). X-ray phase analysis indicates that vernadite holds most of the Mn in the concretions. It is represented by two, relatively weak reflections, with d-values of 2.44 and 1.41 Å (Fig. 1, curve a).

Diffraction study of the sample, heated to 1000°C indicated that most of the Mn-bearing substance was altered into Mn-spinel. It was identified by a diffraction pattern, with d-values of 2.98, 2.55, 2.12, 1.62, 1.49 Å. Much less Mn

occurs in bixbyite ($\text{Mn, Fe}_2\text{O}_3$). This mineral was identified by d values of 2.71, 2.34, 1.72, 1.66, and 1.44 Å (Fig. 1, curve b; Table 2).

(B) Station 675 (9th Cruise of R/V *Dmitrii Mendeleev*) occurs in the Clarion Fracture Zone, NE Pacific Ocean. Terrigenous-pelagic sediments occur here represented by deep water red clays with volcanic ash [6]. $E_h = +615$ mV [10]. Mn in the sediments of the upper part of the section at the station contained 1.47% Mn, 62.9% Fe and c. 0.3% organic carbon. No sulfide matter occurred in samples of this station [10]. The Mn content in muddy pore waters of the top layer around Station 617 was 50 $\mu\text{g/liter}$ [9].

Concretions from Station 617 are of different dimension, of maximum 12 cm diameter, and of various shapes (spherical, oval and somewhat flattened). The concretion density was 5.4 kg/m^2 [2, 3]. In the central parts they occasionally include volcanic ash, fragments of palagonitized basalt and other matter.

Under the microscope, concretions of Sta. 675 displayed complex interior structures. From the outer zone toward the center, the concretions consisted of thin laminae alternating with columnar-globular structures. Ore and nonore (clayey and biogenic-terrigenous)-bearing laminae were interlayered. Globular precipitates dominated the concretion centers.

As among concretions of Sta. 611, thin lenses and laminae occur in various concretion parts at Sta. 675, occasionally at the base of columnar structures and among collomorph substances. They are composed of highly reflective ore matter, characterized, according to microprobe data by high Mn/Fe ratios. The organic C content at Sta. 675 ranged between 0.08-0.12%.

Comparison of major and minor elements in the outer and inner concretion zones indicated great similarity between the Table 1 thus provides mean values of the ore shells [2, 3]. The mineralogy of the concretions at Sta. 675 has been already investigated [17, 18]. The diffraction pattern of the original, unheated initial sample (Fig. 1, curve c) produced reflections of $d = 9.65, 4.81, 3.20$ Å, etc, indicative of an apparent ore mineral phase that may correspond to todorokite, busserite-I, busserite-II, asbolite-busserite [16, 17].

The diffraction patterns of samples heated to 105°C for 2 h showed greatly diminished reflection intensities of $d = 9.65$ and $d = 7.2$ Å (Fig. 11 curve d). This indicated presence of busserite-I, asbolite or asbolite-busserite in the samples. Electron microdiffraction studies refined data of the phase composition at Sta. 675. It indicated the presence of mixed asbolite-busserite and busserite-I. The analyses showed that Fe-vernadite and feroxyhyte [16] were less frequent in the Clarion-Clipperton Zone.

After heated to 1000°C, the concretion sample diffraction patterns from Sta. 675 produced Mn-spinel (4.87, 2.99, 256, etc.) and bixbyite (2.71, 2.35, 1.66, 1.42 Å) reflections (Fig. 1, curve e; Table 2). In addition, the 2.92, 2.51, 2.34, 1.72 and 1.66 Å reflections are near to but not identical with the hausmannite reflection d values. Thus, interlayer distances in the tetragonal unit cell of $a = 5.84$ Å and $c = 9.368$ Å parameters corresponded to crystal indices 200, 211, 004, and 202. Calculated reflections, with respect to these indices produced the 2.921, 2.517, 2.347, and 2.066 Å values, correspondingly. Thus, in contrast with the hausmannite cell ($a = 5.76$ Å; $c = 9.44$ Å), parameter a increased and c decreased in this phase. This may have resulted from partial replacement of Mn^{3+} by Fe^{3+} , in contrast with hausmannite, was due to elimination of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ ratio.

The presence of various phases that formed during heating of given samples was due to various minerals (asbolite-busserite, busserite-I, etc.) in the initial samples that behaved differently in the course of subsequent heating.

(C) The Clarion-Clipperton ore province, in the northeast Pacific, is greatly enriched in Fe–Mn concretions and has been studied by many workers. Many publications describe sediment and ore formation in this area. Only a few are mentioned here. This allows us to remain brief, dealing only with the most important features and characteristics.

The Clarion-Clipperton Province, southeast of the Hawaiian Islands is also part of the Equatorial area, characterized by increased bioproductivity [7, 8]. Mn–Fe concretions, transmitted to us for study (Table 1) were taken in Map Polygon Area #2483 (Station 2483-12).

Station 2483-12 was characterized by exposed Pleistocene sediments, represented basically by diatom-enriched clay-radiolarian-clay muds. As in the area of Station 611 and 675, the sediments were strongly oxidized ($E_h = +450$ -550 mV and higher). The organic content was low (0.25-0.35%). Radiolarian oozes at Sta. 2483-12 contained c. 0.85% organic matter and 3.8% Fe. In Polygon Area 2483, muddy pore waters contained a mean of 17 mg/liter Mn and 20 mg/liter Fe [1].

Various studies [14-16] indicated that in the Clarion-Clipperton Zone busserite-I and busserite-II are the dominant minerals in concretions (Type A). Asbolite-busserite, Fe-vernadite, todorokite, and birnessite developed in the second stage. As suggested in the literature, some of these minerals may be formed by alteration.

The studied Fe–Mn concretions had somewhat compressed forms (length: c. 50 cm, width: 40 cm, height: 20 cm). Large bothroidal features occurred. They were maximum 0.5–1.0 mm in diameter and 0.2–0.3 mm high. The lower concretion surfaces also developed bothroidal features but were characterized by a smaller size. A thin, light-colored muddy film was deposited in the space between low bothroidal tubular features of the lower surface. According to microscopic data, the interior concretion structure, in the Station 2483-12 sample was rather complex. Fragments of older concretions formed the groundmass of the interior, evidently unconformably covered by a superimposed, younger shell. The shell's uneven thickness ranged between 4.5 and 6.0–6.5 mm. The outside of the ore coating was of a columnar-globular structure and the contact between the shell and the older concretion body sharp. The outer part of old concretions was of globular-columnar structure. In contrast with the outside coating, it is characterized by a higher relief. Globular-columnar layers alternate with layers, represented by thinly interlayered globular and massive structures toward the concretion center. The central part of older concretions displayed essentially globular structures. Fractures in the concretions were partially healed. Their marginal zones displayed small disconnected Mn and Fe-hydroxide precipitates, somewhat different in structure and color from the surrounding ore matter.

Chemical analysis data (Table 1) from various concretion parts, Sta. 2483-12 indicated that their Mn, Fe, and trace element content was very similar.

Diffraction patterns from initial, unheated samples from the outer concretion part mark two reflections of nearly identical intensities ($d = 9.6$ and 7.2 Å; Fig. 1, curve f). If the second reflection, as we believe, indicates birnessite, than the $d = 9.6$ Å reflection may correspond to a number of Mn-minerals, as asbolite-buserite, buserite-I and -II, and todorokite. Asbolite is considered to be absent; only Mn-minerals buserite I and II, along with secondary minerals asbolite-buserite, todorokite and numerous other minerals have been identified in Polygon Area 2483. Asbolite was absent.

Diffraction patterns of initial, unheated concretion samples from Sta. 2483-12 displayed wide, relatively intensive reflections of $d = 2.45$ and 1.42 Å values, probably indicative of vernadite (Fig. 1, curve, f).

The area ratio of reflections 9.6 and 7.2 Å, minus background, obtained from a synthetic sample that was compiled by weighted values of ratios, based on analyzed component weights, equaled 1.3. After heating this preparate for 2 h at 105°C (Fig. 1, curve g), the reflection area ratio changed greatly. The area of reflection $d = 9.6$ Å was greatly reduced and reflection $d = 7.2$ Å become dominant. Due to Mn loss in the 9.6 Å phase, the 9.6 Å/ 7.2 Å peak area ratio was now 0.18. The loss, approximately estimated, was calculated as c. 7.2. This indicated the important role a Mn mineral played in the outer part of the concretion. During heating at 105°C for 2 h, it changed into the 7 Å, birnessite phase. By using the cited papers that employed a complex of high-resolution methods, we calculate that before being heated to 1000°C the sample consisted essentially of buserite-I (basic phase), birnessite, and buserite-II.

The heated material from the outer concretion zone of a sample, taken at Sta. 2483-12 indicated that Mn-spinel was the basic mineral that formed in this phase. Its diagnostic reflection 4.87 , 2.99 , 2.54 , 1.62 and 1.49 Å dominated in diffraction curve. As in concretions from Sta. 675, the reflection were identical with those concretions of Sta. 675, and heated to 1000°C .

The diffraction pattern of the initial samples from the middle section of a concretion sampled at Sta. 2483-12 (Fig. 1, curve i) produced two reflections in the low-angle range: an intensive $d = 9.6$ Å and a weak one, $d = 7.1$ Å. The peak area ratio was 6.4. After being heated for 2 h at 105°C , the area ratio declined and remained at 4.4 (Fig. 1, curve 1). Consequently, in contrast with the outer portion of the concretion, buserite-II; not buserite-I played the dominant role. The diffraction pattern of the sample, when heated to 1000°C contained essentially Mn-spinel reflections (Fig. 21, curve m; Table 2).

The inner part of the concretion produced two reflection, 9.6 and 7.2 Å, with an intermediate weak reflection of $d = 8.8$ Å. It probably relates to a mixed-layer birnessite-asbolite phase (Fig. 1, curve n). The area ratio of reflection 9.6 and 7.2 Å equaled 1.5 in the initial sample.

105°C heating for 2 h increased the 7.2 -Å reflection area and reduced the 9.6 -Å reflection peak area (Fig. 1, curve o). After heating, the peak area ratio was 0.23; the area of the 9.6 -Å reflection was reduced 6.5-times.

Diffraction data indicated that both the inner and the outer concretion zone consisted mainly of buserite-I. Buserite-II and birnessite played secondary roles. Addition relatively intensive reflection of $d = 2.44$ and 1.41 Å indicate the presence of vernadite. Electron-microdiffraction data from the inner concretion zone marked the presence of vernadite and Fe-vernadite [11, 16].

After heated to 1000°C , Mn-spinel reflections appeared in the patterns (Fig. 1, curve n, Table 2).

(D) The most representative samples formed through diagenesis, with a relatively high background concentrations of organic matter in hemipelagic ocean sediments, indicated apparent separation of Mn from Fe. This was due to different migration patterns in pore waters and formation of Fe-sulfides as columnar and tubular Mn-oxide nodules at Sta. 82105 on the ocean slope of the Central American Trench [4]. The sediment core at this station was 457 cm long. The enclosing sediment consists of gray aleurolitic mud, with admixed volcanic tuff.

Pyrite was the main authigenic mineral in the lower sediment section. Much smaller amounts of magnetic Fe_3S_4 ; melnikovite (greigite) also occurred. Its concentration increased markedly in the 200-250-cm middle section, while the pyrite content declined. Melnikovite develops mostly from radiolarian tests and was represented by small globular nodules. The upper section (15-25 cm) included almost no Fe-sulfides. Tubular and columnar Mn-oxide nodules were the most widespread, with genetically associated Mn-carbonates of complex composition [21].

Chemical analyses of sediments from various parts of the section indicated that the highest concentrations of organic matter, expressed as Corg, occurred in the upper sediment interval ($C_{\text{org}} = 1.26\%$). The organic matter- and Mn-content declined downward in the section. The highest (1.77%) concentrations occurred between 15-20 cm, the least (0.76-1.1%), in sediments of the lower section. Iron has also undergone active changes in the process. The $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio increased sevenfold, from 0.02 to c. 0.15 downward in the section. The muddy pore waters, squeezed out of the sediments also changed. The Mn content in sediment pore waters of the upper section was 1.9-2.0 mg/liter; in the lower, 0.1 mg/liter. Due to sulfate reduction, the SO_4^{2-} content in the muddy pore waters declined markedly in the lower section.

Columnar and tubular substances from Sta. 82105 consist of Mn-bearing sediments and practically no Fe. Under the microscope they appear as fine-grained, isotropic matter, with crossed nicols. They contain very minute amounts of Ni, Cu, and Co (Table 1).

Diffraction analysis of columnar and tubular nodules indicated that they consist of a 10 Å-Mn mineral, with a series of basal reflection $d_{001} = 9.66/\text{liter } \text{\AA}$ (Fig. 1, curve o).

After heating at 105°C for 2 h, the first low-angle reflection, $d = 9.6 \text{ \AA}$ was shifted to the high-angle field, with $d = 8.8 \text{ \AA}$ (Fig. 1, curve p). An intensive reflection $d = 4.85 \text{ \AA}$, remains practically in place, diminished and broadened. Thus, the x-ray pattern of the heated sample includes an incomplete series of basal reflection, typical of unordered mixed-layer asbolite-buserite [17].

Complex studies by electron microdiffraction, x-ray and other methods, of Mn-oxides of samples from Sta. 82105 indicated that they contain a new variety of asbolite-buserite with disproportionate $\text{Mn}^{4+} - \text{Mn}^{3+}$ layers that formed by active microorganic diagenetic activity [6].

Heating of samples to 1000°C transformed the enclosed layers and formed different hausmannite and Mn-spinel phases (Fig. 1, curve q). These two phases possibly formed by changes in various layers that were part of unordered asbolite-buserite.

(E) We have studied an essentially Mn-bearing hydrothermal crust (Table 1) for comparison purposes. Along with other hydrothermal matter, the crust was dredged from a nameless, small seamount of the South Yamato Range, Sea of Japan. Chemical and spectral analysis data indicated the presence of minor amounts of iron and trace elements (Table 1). Scaly, anisotropic, and birefringent structures occurred under the microscope in the sample. Beautifully preserved idiomorphic feldspar, epidote crystals and crystals of many other minerals were observed.

Diffraction data confirmed that the sample included todorokite with minor amounts of birnessite (Fig. 1, curve l) that remained unchanged when heated at 1050°C for 2 h (Fig. 1, curve s). As other hydrothermal Mn minerals [20], when heated to 1000°C, the todorokite from the Sea of Japan (sample 7783) changed into hausmannite (Fig. 1, curve t, Table 2).

* * * * *

The final alteration products of ore minerals in sedimentary concretions, characterized by variable Mn/Fe ratios and heated at high temperatures in air (maximum 1000°C) belong to two groups:

(1) various concretion-bearing ore types, generally characterized by higher Ni, Cu, and Co content. They formed by (a) hydrogenic (sedimentational) means and contain mostly, probably partly Fe-bearing vernadite. Their Mn/Fe ratios are lower (< 1); (b) by sedimentational-diagenetic means. Main minerals consist of jacobsonite, asbolite-buserite, and buserite-I that are gradational toward birnessite when heated at 105°C in air. Higher Mn/Fe (3.1) ratios characterize them;

(c) by Halbach's "early diagenetic process [21-25]. High (4.5-7.0) Mn/Fe ratios are typical. Type mineral: buserite-I (basic phase). When heated, it becomes slightly transitional toward birnessite and buserite-II. These minerals are independent of the original mineral composition and its Mn/Fe ratios. When heated at high temperatures (maximum 1000°C), the minerals, as sedimentary birnessites with high trace element content [10] do, convert essentially into Mn-spinel.

The second group consist of tubular and columnar concretions that form during diagenesis in the hemipelagic ocean zone in sediments with higher organic content. They contain practically no iron. The Ni, Cu, and Co content is very small. The basic mineral content in the tubular and columnar concretions is asbolite-buserite, with imperfect $\text{Mn}^{4+} - \text{Mn}^{3+}$ layers. Two phases are shown in the diffraction pattern when heated to 1000°C; a hausmannite and a Mn-spinel phase. These reflect the different compositions.

We believe that the data support the assumption [20] that when heated at high-temperatures in air, Fe-Mn concretionary ores provide additional criteria for distinguishing them as sedimentary or hydrothermally created Fe-Mn products [22]. It is important that when various sedimentary Fe-Mn oceanic concretion ore types [23-27]; sedimentary, sedimentary-diagenetic and subdiagenetic ores that formed in pelagic zone sediments with lower organic C content, are heated in air to 1000°C, the heated products display generally great similarities.

This contrasts with the behavior of actual diagenetic substances.

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Fe AND S IN THE SEDIMENTARY PROCESS, OXYGEN-RICH BLACK SEA ZONE. PART II. EARLY SEDIMENT DIAGENESIS AND ITS ROLE IN HOLOCENE SHELF SEDIMENTATION

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The present paper interprets data presented in Part I. The specifics and mechanism of early diagenetic processes, mostly sulfide formation, were investigated on the present Black Sea shelf. Probable diagenetic conditions in various Holocene time intervals are also discussed.

My previous paper [6] presented data on the concentration of reactive Fe and reducing S forms in Holocene deposits on the Black Sea shelf. Two major aspects require interpretation. First, the distribution patterns of the studied components (FeS_2 , S^{2-} , S^0 , organic S, $\text{SO}_{4(\text{p-p})}^{2-}$, total reactive Fe, organic C, CaCO_3 , H_2O , and E_{Pt} values) in the upper sediment layer reveal the currently active diagenetic process in these beds. Second, the data allow reconstruction of shelf sedimentation conditions and diagenesis during various Holocene intervals.

Basic theoretical assumptions on the development of early diagenesis in marine sediments and the impact in the oxygen-rich Black Sea zone have been discussed earlier [6]. One of the necessary development conditions for this process (a reducing one, with respect to the original Fe(III) and $\text{S}_{\text{SO}_4}^{2-}$) involves the preliminary aerobic oxidizing digestion of organic matter (OM). This geochemical treatment formed a limited group of reactive and microbiologically assimilated organic matter (OM) forms. Active bacterial sulfate reduction and Fe(III) reduction followed this. This indicates that the aeration regime of sediments is a very important factor that controls early diagenetic processes, along with the amount and composition of the introduced organic matter. Detailed study of the development conditions of these processes on the Black Sea shelf are essential in the study of diagenesis under varied natural conditions. These conditions involve periodic oxygen deficit in bottom waters and intensive reworking of the seafloor sediment layer.

THE EARLY DIAGENETIC PROCESS IN SHELF FLOOR DEPOSITS

Numerous questions of various categories arose in this study from the obtained data [6]. The most significant involved a factor that controlled increases in the concentration of the universally present pyrite, downward from the seafloor in the sediment section. The concentration increase is of near-linear character. Initial pyrite accumulation, with minimum FeS_2 values, commonly is associated with the sediment surface. Significant variations in the thickness of the associated horizons (from 10-15 cm, to 1-1.5 m), the ambiguous relationship that effects the distribution of other sediment components represent additional important characteristics.

These effects include episodic enrichment of seafloor layers both in sulfide and native S, and in reactive and detrital forms of Fe. A typical rhythmic distribution pattern of the components occurs against a general background of increased FeS_2 content.

These characteristics are clearly displayed in the entire studied area. The majority of the most typical and best definable forms occur in the core of Station 861 on the Bulgarian shelf [6] at 69 m depth. This unit is composed entirely of recent (Late Holocene, Hl_{III}) deposits. Figure 1 indicates the component distribution in the upper core interval.

Increased total pyrite content occurs in the upper part of the c. 40-cm horizon. The horizon also limits the increase in the total reactive Fe content in the section. This component slightly increases toward the seafloor within the section. The horizon consists of an upper(I) and lower(II) subunit.

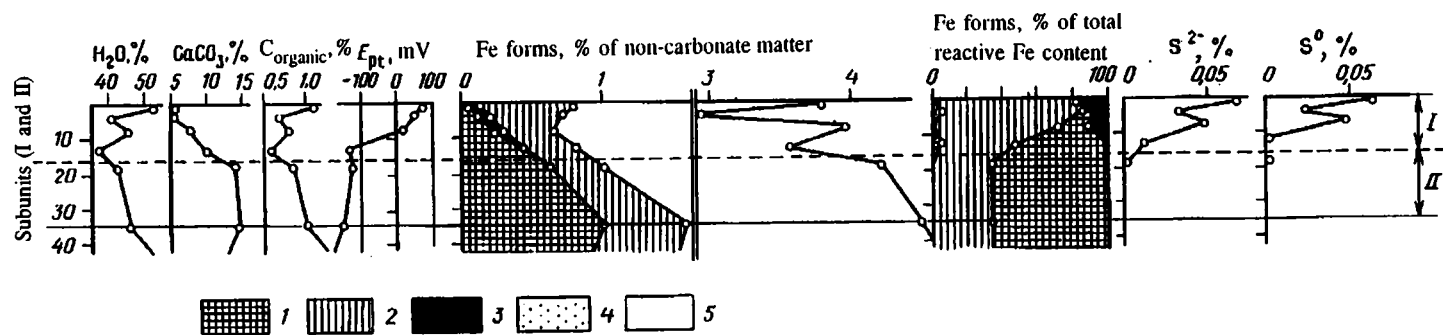


Fig. 1. Component distribution in upper shelf sediment subunit (Sta. 861, 69 m depth; coordinates $43^{\circ}00.6' \text{ N}$, $28^{\circ}23.2' \text{ E}$). 1-5) Fe forms (1 - pyrite Fe; 2 - nonsulfide Fe(II); 3 - Hydrotroilite Fe; 4 - reactive Fe(III); 5 - detrital forms); I, II) subunits within seafloor horizon.

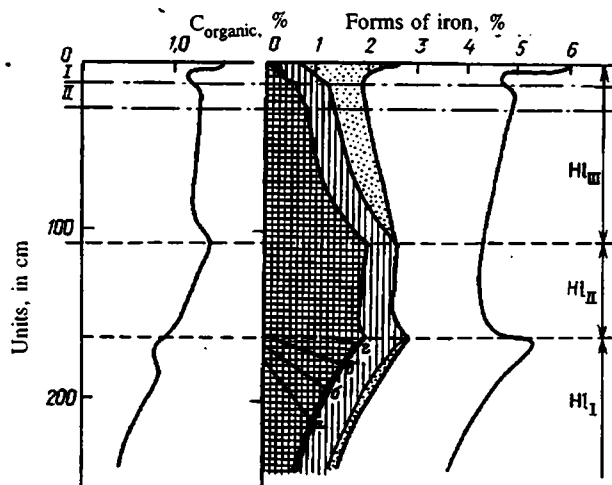


Fig. 2. Distribution characteristics of components in Holocene shelf deposits. Stratigraphic units: HI_I – Late Novoeuxinic; HI_{II} – Early Black Sea; HI_{III} – Late Holocene (Recent); a, b, c, d) assumed changes in the Fe_{pyrite} profile, relative to the surface of Novoeuxinic sediments at the transition from the Novoeuxinic to the Early Black Sea depositional regime. I) reworked surface sediment subunit I; II) zone of aeration diffusion on recent shelf. Fe symbols: as in Fig. 1.

The upper subunit (0-to-15-20 cm) contains increased total FeS₂ content, corresponding to a linear increase in the total Fe_{pyrite} content from c. 2%, to c. 65%. In addition to Fe_{pyr}, the total reactive forms include mostly bivalent non-sulfide Fe. Its maximum occurs at the sediment surface. Small, variable amounts of reactive Fe(III) also occur in the upper subunit (<5% of the total reactive Fe content). Acid-soluble Fe-sulfides (Fe-hydrotroilite) are also present. Maximum Fe-hydrotroilite content, c.10-15% of total reactive Fe also occur in the sediment surface.

In addition to sulfide S²⁻, associated with hydrotroilite iron, similar amounts of S⁰ were also present in the subunit. Although greater than in the underlying sediments, the total S²⁻ and S⁰ content was minor (0.06-0.07%). S²⁻ and S⁰ concentrations were variable in laminae within the upper subunit, allowing excellent correlation between them. Rhythmic patterns in this section characterize not only S²⁻ and S⁰ but also many other components: detrital Fe, organic C, H₂O, and Fe(III) within the total reactive Fe content. A linear increase in components takes place downward in the carbonate section.

The controversial nature of E_{pt} values is of special interest. Maximum positive E_{pt} values (+70 mV) correlate with maxima of reducing forms of S²⁻ and Fe(II) in sediments of the studied core at the sediment-bottom water interface. Reduced E_{pt} values in the upper subunit correspond to a decrease of this form in the sediments. This reflects the general disequilibrium of the mineral-forming medium in sediments of the upper (I) subunit and the metastable nature of sulfide and nonsulfide compounds in the reactive iron content.

The components display a less complex character in the lower (II) subunit (Fig. 1). It is 20 cm thick and the total FeS₂ and reactive Fe content continue a downward increase. However, the Fe_{pyr} ratio within the total reactive iron content remains constant. Sulfide and native sulfur are almost absent and the E_{pt} value declines sharply.

These data generally indicate a sharp difference in the character of the diagenetic process within the subunits and require an explanation with respect to the physicochemical aspects of the difference.

None of the distribution characteristics of the sediment units suggest presence or absence of diagenetic alteration processes at the time. They provide no information on kinetic parameters. Chemical analysis results indicate only the relative nature of the process that is valid only if the theoretical assumptions are based soundly. In comparison with other cores, our data base (Fig. 1, Station 861) is rather impressive. In our case, component distribution patterns in the 10-15-cm seafloor layer, typical of all the studied shelf areas, are associated with an unusual component distribution pattern in the underlying Late Holocene beds. This fact significantly facilitates the data interpretation.

Most studied components; primarily the total reactive iron content and its subcomponents have rather constant concentrations in the unit that underlies the upper, 40-cm subunit. Only the detrital forms of iron display significant

variations. With a constant total reactive iron content the corresponding total iron content fluctuates within c. 1%. The E_{Pt} values also vary. After a sharp decline in the surface layer, from +70 mV to -150 mV, it increased again downward in the section, to -50 mV at c. 180 cm depth.

The steady concentrations of basic components, as $CaCO_3$, organic carbon, H_2O total reactive Fe, and its subcomponents, as well as the lithological uniformity of the sediments indicate a stability in Late Holocene (Recent) depositional regime and sediment diagenesis in this region. The reducing Fe-S-complex thus corresponds to a regime that formed in the seafloor layer, 40 cm thick at most. Below this horizon, theoretically only a very slow and homogeneous diagenetic process may occur throughout the sequence. It does not include significant concentrations of the total reactive iron and total H_2S -sulfur content.

In interpreting the component distribution pattern in the top horizon (Fig. 1), one must first evaluate the impact of redistribution of the surface sediment matter by bottom currents. An individual case of redeposition in simplest terms indicates sediment transfer from the top layer into suspension, with subsequent repeated sediment accumulation. Approximate quantitative calculations of the redeposition intensity, based on direct observations by submarine instruments, indicate that at c. 100 m depth the seafloor layer is eroded at least once a year. This is followed by annual redeposition of a c. 10-cm-thick bottom layer [1, 2]. Thinner beds apparently are reworked more frequently.

Sediments studied in Station 861 and surface deposits of other studied Black Sea shelf area were characterized by very minor oxidation of the layers. A ≤ 1 -mm-thick, partially eroded oxidized film appears. Increase in the FeS_2 content starts practically from the seafloor surface. For this reason, part of the pyrite and all other diagenetically formed reduced components of the upper sediment layer would inevitably be involved in the redeposition process and exposed to intensive oxidation by oxygen-rich bottom waters. A corresponding increase takes place in the aeration of underlying layer. Clearly, reformation of the universally present pyrite is accomplished both by the continuous FeS_2 accumulation in the diagenetic process and by its partial oxidation by dissolved oxygen. Direct or indirect oxygen participation, via Fe(III) and S^0 , and in pyrite formation ($2S^{2-} - 2e \rightarrow S_2^{2-}$ [7]) seem to involve diagenetic FeS_2 formation in sediments within areas of optimum $O_{2(p-p)}$ concentration. Thus the pyrite distribution is of a dynamic nature and reflect changes in the formation intensities and FeS_2 oxidation in the sediment section.

At first glance, pyrite formation is incompatible with the presence of easily oxidizable, reduced forms of S^{2-} (Fig. 1) as well as of sulfide and nonsulfide ferrous iron in the upper subunit (I). This contradiction is easily resolved if the episodic character of the sediment reworking in the upper subunit is considered, along with observations on individual phases in the process. This allows satisfactory explanation of nearly all data from the upper subunit.

During redeposition in oxygenated bottom waters (mixing, redeposition and resuspension), oxidation of the earlier deposited, reduced chemical forms are taken into account in conjunction with their stability in the presence of O_2 during interaction between components. These phases generally result in an almost complete oxidation of sulfide S, associated with nonsulfide Fe(II) that did not enter the silicate lattice structures, remaining stable in the presence of O_2 . It also indicate partial oxidation of the pyrite and S^0 with regard to the $O_{2(p-p)}$ concentrations. At this time did the aerobic mineralization process of the dispersed organic matter become active. To varying degrees, also related to O_2 concentrations, it was associated with accumulation of intermediate, reactive oxidizing and microbiologically assimilated forms of

organic matter: assimilated OM = initial OM $\xrightarrow{O_2}$ assimilated OM $\rightarrow CO_2$. At the same time, aeration increased in the underlying unit to a certain depth. Most significantly, the reworking process involves sediment fractionation, including all diagenetically formed products on the basis of granulometry, density and surface characteristics of dispersed particles that include these compounds. This circumstance produced the pattern in subunit I, needed for the rhythmic distribution for most of the investigated components (Fig. 1). It was determined mostly by a time-frequency deposition spectrum of seafloor layers of various thickness values. The spectrum explains the variety, variability and episodic character of the individual effects of this distribution very well [6]. Fractionation of reactive iron forms apparently does not exclude the possibility that the oxidized layers may become enriched in these forms also by diffusional-diagenetic reworking.

During the inactive phase intensive reducing processes are again initiated in the repeatedly redeposited seafloor layer. This documents the oxidation and fractionation history of sediments on the basis of the accumulated assimilated OM. Oxygen consumption by muddy pore waters in this horizon during oxidation of the dispersed OM in the sediments leads to formation of anaerobic microzones and of reduced forms of Fe and S. In general, this forms an integrated diffusional $O_{2(p-p)}$ flux, directed from the bottom waters into the sediments. It conforms to the diffusion conditions of its distribution

profile. An oxygen concentration area develops. It is sufficient to support local flux to reach the microzone boundaries. This explains on the one hand the regeneration of the assimilated OM; on the other, partial oxidation of reducing forms of Fe and S. Due to oxidation of sulfide ($2S^{2-} - 2e \rightarrow S_2^{2-}$) and in conjunction with further oxidation to the sulfate stage, pyrite-S accumulates under these conditions. Diminishing $O_{2(p-p)}$ concentrations downward in the section result in steadily increasing amounts of pyrite, unable to oxidize. This results in increased FeS_2 content downward in the section. In this particular aeration phase, the trend correlates with the $O_{2(p-p)}$ distribution pattern in the section.

As shown by the downward increasing Fe_{pyr} values within the total reactive Fe concentration in the section, pyrite formation mostly involves the total reactive iron content. One should not completely dismiss the possibility that crystallized iron forms play a role in this process. The basic portion of reactive Fe(III) that enters sediments through deposition or through the diagenetic process of a previous stage, was converted in the developing microzones into a chemical and microbiological reduction product via aerobic and anaerobic hydrolytic disintegration of the organic matter. This process is instrumental in the sulfate reduction process [6]. The following equilibria occur on the boundary of anaerobic micro-

zones: reactive Fe(III) $\xrightleftharpoons[O_2]{OM}$ reactive Fe(II) Oxygen or oxidized forms ($Fe(III)$, S^0) participate in pyrite formation. It may,

therefore, be assumed that even mobile reducing microzone boundaries conform to this mostly spatially defined process. Its products are independent of iron reduction-produced bacterial hydrogen sulfide diffused to this boundary. Interaction with all component products of the above equations are inevitable. Thus, the chemical mechanism of early diagenetic pyrite formation is considered within the framework of a given functioning quasiequilibrium regime of an oxidizing-reducing biochemical system (OM - O_2 - Fe - S). It includes various valence forms of Fe and S: $Fe(III)$, $Fe(II)$, S^{2-} and S^0 .

With a steady $O_{2(p-p)}$ diffusional flux from the bottom waters and during its consumption, in the sediments, the increased FeS_2 content may reflect a stabilized balancing process. Simultaneously with pyrite formation, regeneration of assimilated OM, limited by oxygen influx, takes place. Under special Black Sea shelf conditions, the seafloor horizon from the start contains certain amounts of assimilated OM. It is periodically, during aeration in suspended state, enriched on account of the redeposition process. As a rule, this process is more favorable than diffusional aeration of sediments that rest on the bottom. For this reason, reduction of $Fe(III)$ and bacterial sulfate reduction in anaerobic microzones of the seafloor layer continue with significant intensity, until the assimilated organic matter is exhausted. Further accumulation of reducing, mostly mobile forms of iron and sulfur ($Fe_{(p-p)}^{2+}$, $HS_{(p-p)}^-$) and corresponding accumulation of $O_{2(p-p)}$ during their oxidation generally lead to anaerobic conditions in the sediments. Pyrite accumulation under these conditions is sharply reduced and becomes feasible only from residual $Fe(III)$. Apparently, it is limited. FeS_2 does occur in the section but as H_2S is separated out, its effect on reactive forms of $Fe(II)$ and $Fe(III)$ takes mostly place through formation of hydrotroilite-poorly crystallized sulfide phases of iron with different valences and variable composition. The phase composition depends on ratios between these forms and on conditions of their interaction (pH, t, S, etc.). The amount of hydrotroilite under these conditions, is small and may not be significant because the anaerobic conditions that result from this concentration stop the regeneration of assimilated organic matter. This leads to attenuated sulfate reduction. Clearly, in the presence of sufficient assimilated organic content, very minor amounts of free H_2S may have accumulated in this stage after inclusion of the reactive Fe into hydrotroilite.

This indicates not only the quantitative relationships with the sulfide phases but also their distribution characteristics within the section (Fig. 1). FeS_2 formation is limited by the influx of $O_{2(p-p)}$. Therefore, the linear pyrite profile does not indicate any relationship with the unevenly distributed organic matter that accumulates through sediment fractionation. Hydrotroilite formation is limited by the intensity and continuity of sulfate reduction under severely anaerobic conditions. At this time was the assimilated OM supply proportional to the initial organic matter content and, correspondingly, to the residual organic C content. Due to these relationships, there is a positive correlation between organic C and microquantities of S^{2-} (Fig. 1). This interrelationship, developed due to the oxidation of part of the sulfide S by residual oxygen or reactive $Fe(III)$ in the formative stage in sediments, subjected to highly anaerobic conditions, also occurred between S^{2-} and S^0 .

Formation of anaerobic conditions in the seafloor beds in parts of the Black Sea shelf may be directly related to the introduction of oxygen-free waters from the deep basin. However, the rhythmic nature of the diagenetic process in these beds apparently was controlled mostly by the rhythmic nature of reworking. It is characterized by much greater frequency and due to their different origin, its formation did not coincide with times of periodic shelf aeration. Sediment reworking

was due to wave-related reworking of the upper shelf zone, while oxygen-free waters were introduced by the basic counterclockwise currents.

These circumstances apply to upper subunit I and identify the subunit as composed of actively reworked sediments. In evaluating the role of this reworking, one should also note the possible reworking of certain components, that similar to FeS_2 , was directly due to the physical fractionation of particles of given density and dispersive characteristics. The linear downward increase in CaCO_3 content (Fig. 1) in subunit I may be attributable to this factor. Pyrite may also become fractionated in oxygen-free bottom waters.

The lower unit, subzone II, displayed the highest $\text{Fe}_{\text{pyrite}}$ content in the core, within the total reactive iron content. The end of further increases in its concentration values indicate the exhaustion of the reactive iron content that allows FeS_2 formation. As the result, the absence of reactive Fe(III) in the sediments also precluded ongoing pyrite development. For this reason, only a very minor diagenetic reworking of detrital forms of iron may take place in subunit II under highly anoxic conditions; with very minor supply of assimilated OM and products of slow, hydrolithic decomposition of the OM. Thus, increase in the total pyrite content downward in the section is unrelated to any ongoing formation of pyrite in subunit II. Apparently, this reflects certain changes in sediment accumulation. As shown by the lithological logs, this fact is indicated by the unique directions in segments of the corresponding organic C and total Fe curves (Fig. 1). In comparison with the underlying beds, it is similarly demonstrated by an increase in the total thickness of sand and silt layers in the upper horizon. The component distribution in lower subunit, II, may result from sediment fractionation during one of the rare redeposition episodes that involved the maximum c. 40 cm horizon. This is a highly likely scenario in the middle shelf zone.

Sharp differences in the diagenetic reworking of Fe- and S-compounds in the two units of the interval correspond to significant differences in the microbiological conditions of OM and to the reactive capabilities of Fe form in sediments of these subunits. Active regeneration of assimilated OM and reactive Fe in the continuous regeneration of the upper layer indicate that early diagenetic reorganization of the Black Sea shelf deposits was limited almost entirely to this zone. Most of the assimilated OM in underlying sediments of the lower subunit has already been consumed and the available reactive Fe used up in pyrite development. They may only be reproduced during brief increases in the diffusional $\text{O}_{2(\text{p-p})}$ flux during brief episodes when the upper layer is reworked. As the result, during the rest of the time intensive reducing processes shield sediments from O_2 . This demonstrates well the impact that seafloor sediment mobility has, and the hydrodynamic effects of bottom waters on the evolution of the early diagenetic regime in the studied sediments.

Conditions at Sta. 861 in the middle shelf area (69 m depth), typically include maximum thickness values for the reworked upper horizons. In other studied areas, as Kalamitsk Bay and the Anatolian Shelf [6], only the thin upper part of the pyrite growth profile undergoes intensive diagenetic changes. The significant lower interval either formed during the quiescent stage or reflects changing depositional and diagenetic conditions during the Late Holocene.

In deposits of Station 861 the boundary of the active diagenetic layer is defined very sharply. At other stations, the layer is marked by a clearcut discontinuity in the $\text{Fe}_{\text{pyr/total}}$ reactive Fe curves. As an example, the core of the shallowest Station 797 of the Kalamitsk shelf reflects an active pyrite formation stage in a c. 30-cm interval. This is indicated by a sharp decline in the reactive Fe(III) content, an increased pyrite iron content in the total reactive iron concentration and, possibly, by the presence of hydrotroilitic pigmentation (S^{2-} c. 0.02%) in the underlying sediments. This bed is maximum 20-30 cm thick at Sta. 800. In that case, the zone of active sulfate reduction corresponds to a sub-seafloor $\text{S}_{\text{SO}_4}^{2-}$ -minimum in the muddy pore waters and thus to the greatest sulfate demand in the process [6]. The periodically aerated unit in this region may reach c. 60-cm. It is marked by a sharp break in the S_{pyrite} curve. The ongoing diagenetic process in deepest Sta. 795 corresponds to the sharp pyrite profile in a 0-15-cm-thick bed. Sulfide S is absent from this unit but S_0 does occur. This apparently indicates the moderate aeration of the unit. An active aeration stage apparently impacts the seafloor horizon (0-15 cm) in Sta. 822, Anatolian Shelf [6]. It marks initiation of the FeS_2 profile. The rhythmic distribution of S^0 in this sediment unit may have resulted from the reworking of thinner beds. Thus, none of the noted component distribution effects contradict the suggested interpretation on the diagenesis of Black Sea shelf deposits.

The E_{Pt} -distribution pattern plays an important role in our data (Fig. 1). Values of the Pt electrode potential are variable in freshly sampled sediments and determined by the presence of certain reducing or oxidizing element forms, primarily in muddy water solutions, unavoidable impacted by the suspension effect [3]. In the absence of $\text{O}_{2(\text{p-p})}$, in the muddy pore waters of the upper layer and in the given stage of the process, the declining E_{Pt} values in this layer may point primarily to a downward increase in $\text{Fe}_{(\text{p-p})}^{2+}$ concentrations. The coincidence of maximum positive E_{Pt} values and maximum values of Fe(II) and S^{2-} in the upper part of the layer indicate that interaction between these components and

the Pt electrode became more difficult. They were mostly converted into solid sediments. This is an entirely natural process for Fe(II) and S^{2-} , associated with the sulfide compounds that are not readily soluble. With regard to nonsulfide Fe(II), this coincidence suggests that the reduction of reactive Fe(III) in the surface horizon does not accompany entry of Fe^{2+} into the solution. The entry is possible only if the reactive Fe(III) in basic amorphous hydroxides is strongly combined with diagenetically active OM of the same area. That is, it takes place as organic-mineral particles and aggregates that provide the potential of combining chemically and through sorption with Fe^{2+} .

The inevitable development of these aggregates was noted when analyzing results of deep basin deposits [5]. High surface activity characterizes dispersed particles that contain organic matter and iron. The activity is of colloidal-chemical and complex-forming nature. Organic matter and iron are incorporated into the particles during the aerobic oxidizing-

reducing microbiological reconstitution of the suspension: $OM \xrightarrow{O_2} \text{assimilated OM}, \text{detrital Fe(III)} \xrightarrow{OM} \text{Fe(III)} \xrightarrow{O_2} \text{reactive Fe(III)}$. In this case these aggregates do not only enter the sediment from the water of bioproductive zones, but also actively form by redeposition and remixing with bottom sediment matter. Further transport of these unstable substances takes place in two directions.

When remaining in sediments, they quickly decompose, at the rate of consumption of organic matter in the diagenetic process. Pyritization of reactive Fe, dehydration and aging of the initial gel-like thixotropic structures takes place. The associated Fe^{2+} obtains mobility from the muddy water solution and the opportunity to interact with the surface of the Pt electrode. This is also expressed in declining E_{Pt} values in the surface deposit section. Further steady increase in the E_{Pt} values along the Late Holocene section apparently indicates a slow combination with minute amounts of $Fe_{(p-p)}^{2+}$ in silicate and Al-silicate forms [6].

In the bottom water transport of these aggregate types from shelf to basin, in the absence of oxygen or its deficit the particles transport certain amounts diagenetic components that formed on the shelf. These primarily include pyrite, thus explaining the major role reducing Fe and S forms play in the accumulation of deep water sediments. Transport in oxygen-rich waters assumes that, due to the presence of assimilated organic matter and reactive Fe(III), reducing conditions may have been preserved in these particles. Settling under optimal aeration conditions in transitional marine water layers, a large portion of the coagulates, corresponding to their size and effective density, continues to function as suspended microzones of sulfate reduction. Due to aggregation and pyrite formation during accumulation they lose their sedimentational stability and settle according to the hydrologic conditions of the hydrogen sulfide zone. Due to their abrupt attenuation under highly anaerobic conditions, both sulfate and Fe(III) reduction, during their transition into a slower stage, it may be assumed that this oxidation-reduction process that reconstitutes suspensions in the transitional zone of the water layer is mostly controlled by development of a reducing complex of Fe and S species in deep basin sediments. This conclusion was reached independently also through the analysis of interactive relationships between various Fe and S forms in deep water sediment intervals [5].

Our data helped to describe the geochemical mechanism that governs the link between the sediment aeration impact and the diagenetic alteration regime. Under normal sediment aeration conditions, this factor, regionally links the impacted area with effects of dissolved optimal oxygen concentration on OM. This generally forms sediment zones that are markedly different in composition and energy base of the processes and, correspondingly, also in kinetic parameters and productivity.

The most intensive aeration in the upper, oxidized layer is due not only to diffusional oxygen introduction from bottom waters but also to significant periodic reactivation by redeposition and remixing of seafloor sediment matter by bottom currents and influence of the benthos. This is manifested by the presence of active aerobic oxidizing mineralization, sufficient for limiting reducing processes. The mean $O_{2(p-p)}$ content was sufficient to suppress reducing processes. Active

aerobic oxidizing mineralization of the organic matter ($OM \xrightarrow{O_2} OM_{\text{assim}} \xrightarrow{O_2} CO_2$) was unaccompanied by required intermediate assimilated OM. only small amounts of reducing forms of Fe and S formed. They almost completely became oxidized.

A gradually deeper penetrating diffusional influx of $O_{2(p-p)}$ into the reduced sediment bed limits oxidation of the intermediate, assimilated OM. This leads to their accumulation and formation of anaerobic microzones and the developing reducing processes in them. Pyrite and nonsulfide-Fe(II) represent the basic final products of these processes in $O_{2(p-p)}$ concentration zones and in the associated sediment horizon. The pyrite in the accumulation profile may be considered a

quasi-equilibrium product that corresponds to associated reactions, optimal for the system ($2S^{2-} - 2e^- \rightarrow S_2^{2-} - 14e^- \rightarrow 2S^{6+}$). These control oxygen flux, the oxidizing effects of which in the first stage may function through combination with Fe(III) and S^0 . The chemical and physicochemical aspects of pyrite formation require further studies. The FeS_2 accumulative profile is dynamic and variable in time. Such changes depend on the diffusional $O_{2(p-p)}$ flux, controlled primarily by the redeposition regime of seafloor sediment units. Thus, the kinetics of pyrite formation is associated with mean sediment accumulation rate that can be calculated by geochronology methods. With stable accumulation rates and constant aeration values through geological time, one may quite reliably correlate mean rates of FeS_2 accumulation in sediments. However, such conditions are very rare.

In sediments that underlie the pyrite accumulation profile, diffusional $O_{2(p-p)}$ microfluxes were unavailable for compensation. This generally resulted in more intensively anaerobic conditions in the sediment unit. Regeneration of assimilated organic matter ceased. Reducing processes, based mostly on the supply of organic matter that formed during aeration, quickly ceased as organic supply stopped. Subsequently, a decaying, very weak diagenetic process may have continued in the thick sediment unit. It was based on chemically varied hydrolithic anaerobic decomposition products of the organic matter and on the kinetics that controlled decomposition. This stage caused practically no change in the total and relative concentration values of associated Fe and S forms in the upper layers.

It is emphasized that the FeS_2 accumulative profile is dynamic in time. It is subjected to changes, with changes in the diffusional $O_{2(p-p)}$ flux, in turn primarily controlled by a regime of redeposition in seafloor beds. Thus, pyrite formation kinetics are related to mean sedimentation rates, calculated by absolute age dates. The rates are unchanged even when aeration regime is stable. one may safely correlate mean FeS_2 accretion rates in sediments.

The specific reasons for their development in Black Sea shelf deposits become clear after these zones of diagenetic alteration have been studied. Conditions of steady or periodic O_2 deficit in bottom waters correspond to a general reduction in the thickness of sediments that were involved. This fact assumes reduced thicknesses both in the upper oxidized layer, degraded into a thin oxidized film, and also in the layer of the most productive diagenetic processes that involved pyrite accumulation. The layer's position near/at the seafloor-bottom water interface indicates its complete or partial association with the seafloor surface zone in this area of active sediment redistribution.

Diagenetic processes in this regime were consequently directly controlled by rhythmic redeposition processes, resulting in periodic shifts in sediment aeration in the zone. The shifts started with an active oxidation phase of reduced forms of Fe and S, continuing through formation of the FeS_2 profile, and ending with the attenuation phase that involved formation of certain amount of hydrotroilite, probably also of H_2S that was sufficient for establishing highly anaerobic conditions.

The corresponding sediment unit that underlies this condensed horizon of active diagenetic alterations formed during the weakest anaerobic process failed to significantly impact total S_{H_2S} and total reactive Fe concentrations in the sediments. In this instance, the component distribution patterns in Holocene shelf sediment sections adequately express changes under Holocene sedimentation and diagenetic conditions, thus justifying our attempts to accurately visualize these conditions.

EVOLUTION OF DIAGENETIC CONDITIONS IN SHELF SEDIMENTS THROUGHOUT THE HOLOCENE

In identifying Holocene distribution patterns of Fe- and S-forms, with the exception of the seafloor sediment horizon, the highest level of reduction in each unit generally coincides with an active diagenetic stage the operating conditions of which correspond to conditions of sediment accumulation. Any attempt at detailed explanation as to how concentrations and ratios of the Fe- and S-forms influence these conditions, as well as data interpretation in any given section faces difficulties. This is caused by the absence of a single indicator that would be capable of describing the function of the OM - O_2 - Fe - S biochemical system as whole, and the physicochemical mechanism of pyrite formation in particular. Nevertheless, many typical features of composition distribution have been well explained by previously noted theories. Summarized in Fig. 2, they generally reflect the evolution of depositional conditions in the middle of the Crimean Kalamitsk shelf and in the marginal zone of the Anatolian shelf (Station 800; 119 m depth; Sta. 822, 99 m depth [6]).

The last stage of the Late Novoeuxinic (H₁) interval was characterized by gradual increase in reactive forms of Fe and by a constant increase in the detrital forms. Upward increase in the section of the total iron content correlated perfectly with a pyrite content increase while the total content of nonsulfide Fe(II) remained unchanged. Similarly, the residual organic carbon increased upward in the section, with apparently some decline in the horizon directly beneath the Early Black Sea unit. It possessed a maximum FeS₂ content. very minor amounts of reactive Fe(III)-hydrolysis products also occurred in the Late Novoeuxinic deposits as far upward as the lithological boundary with the Early Black Sea unit.

The data thus indicate that diffusion did not participate in the Novoeuxinic sulfide mineralization. Conditions during the early diagenetic stage were as follows.

Depositional conditions in the Black Sea at the start of this period are quite well known [8]. As the Late Novoeuxinic basin freshened, c. 0.1-0.2% Sphalerite accumulated in shelf sediments during early diagenesis. The low bioproductivity of the shelf, its shallower nature and absence of H₂S influx in the water layer were attributed to a more active aeration regime on the seafloor than the present one. Due to the flux of deep, O_{2(p-p)}-depleted basin waters, there was oxygen deficit. A clearly defined oxygen-rich upper layer and a thick, pyrite-accumulating horizon prevailed. Seafloor sediment reworking thus did not directly impact early diagenesis. only the flux of diffusional O_{2(p-p)} varied in the sediments. Correspondingly, the observed ratios between forms of Fe and S were related to the discussed microzonal oxidizing-reducing pattern. Such diffusional aeration conforms well with our previously discussed body of findings (Fig. 2, H₁).

Minute amounts of reactive Fe(III) and the steady concentration of detrital Fe in the horizon are in agreement with the distribution pattern in which detrital Fe is not significantly involved in the oxidational reconstitution of sediments. The reactive Fe is almost totally reworked. The initial total Fe content thus limits the early diagenetic process. This happens when sufficient amounts of organic matter accumulate and provide a medium for active anaerobic oxidation (initial

OM → assimilated OM). Sulfate reduction occurs within the anaerobic microzone until microbiologically assimilated forms of organic matter are regenerated; that is, until optimal aeration conditions of the original organic matter appear. As earlier discussed, these conditions occur by autoregulation, due to two conflicting and interdependent processes. On the one hand, organic matter oxidizes and reducing forms of Fe and S are diffused by O₂; on the other, development of these reducing forms is initiated by impact of O_{2(p-p)} on organic matter. Correspondingly, the diffusional O₂ flux that impacts sediments is controlled by the decomposition. It takes primarily place through oxidation of associated bacterial H₂S in pyrite that is relatively stable with respect to O₂. The process lasts as long as iron, convertible to pyrite, is also present.

The very small reactive Fe(III) and the stable detrital iron content in the section correspond to a distribution event. During that event, detrital forms of iron were not significantly involved in the oxidation-reduction reconstitution. Although reactive Fe was almost completely reworked. At this time, the initial values of the total reactive Fe limited development of the early diagenetic process. This condition involved sufficient amounts of organic matter in the sediments, providing potential for active aerobic oxidation (initial OM, organic matter assimilated OM). Sulfate-reduction under such conditions occurs in anaerobic microzones as long as the conditions for regeneration for microbiologically assimilated forms (assimilated organic matter) prevail. That is, until optimal conditions for aeration of the initial organic matter exist. As earlier shown, these conditions are superimposed through autoregulation by two counteractive, but interdependent processes. on one side, oxidation of OM and reduction of Fe and S forms are initiated by the impact of O_{2(p-p)} on OM. Correspondingly, diffusive O₂-fluxes in the sediment are controlled by the oxygen consumption regime and supported primarily by oxidation and association of bacterial H₂S with pyrite that is relatively stable with respect to O₂. This happens as long as iron, available for pyritization of Fe, is still present in the sediments. As this reactive Fe is exhausted, free H₂S accumulates in microzones, organic matter is isolated from oxygen influence and SO₄-reduction slows. This condition in the sediment beds correlates with conditions at the base of the FeS₂-accumulation profile and highly anaerobic conditions. A rhythmic regime of diffusional aeration, developed by reworking of seafloor beds, inevitably includes the final phase of

the oxidation process (OM $\xrightarrow{O_2}$ assimilated OM, Fe(II) $\xrightarrow{O_2}$ Fe(III), S²⁻ $\xrightarrow{O_2}$ S_{pyrite}, etc.). These apparently include microzonally distributed trivalent reactive hydrotroilite, formed during development of assimilated forms of organic matter and traces of free H₂S that remained in equilibrium with sulfide and nonsulfide forms of iron.

These patterns persisted throughout the entire studied Late Novoeuxinic period of deposition. However, near the period's end, conditions of early diagenesis changed significantly. The relative stability of detrital Fe in the H₁ section [6] (Fig. 2) indicates an upward increase in the reactive iron content. This is not only due increased terrigenous matter influx,

made possible by a transgression and climatic warming, but also through introduction of deep basin water into the shelf zone from the basin that was depleted in oxygen. Along with biogenic elements, it was also enriched in reactive forms of iron ($\text{Fe}_{(p-p)}^{2+}$, Fe(II) and Fe(III) in stable suspendate). This condition corresponds well to the general scheme of the Black Sea's geochemical evolution. It correlates with a period that immediately preceded the Early Black Sea bioproduction stage, characterized by increased vertical water exchange and coinciding with the start of displacement of fresh waters by denser Mediterranean water in the Novoeuxinic Basin [8]. The reduced Fe was altered by oxidation in the upper water layers and entered shelf deposits as the diagenetically most active amorphous reactive Fe(III) hydroxides. At the same time, the increased supply of biogenic elements to the photic zone led to gradual increase in bioproduktivty on the shelf and corresponding inclusion of organic matter in the sediments. This is shown by upward increase in the residual organic C content (Fig. 2).

Clearly, the most important changes in conditions of the early diagenetic process correspond to the transition from the Novoeuxinic to the Early Black Sea period of deposition. Following Strakhov [8] who described the period in general, we assume that vertical water exchange, typical of the Novoeuxinic Basin was supported and driven by land runoff of glacial origin. From the beginning it was augmented by salt water intrusion. That entered and filled the basin bottom from the Straits of Bosphorus. Later, this influx was supplemented by emergence of deep Novoeuxinic waters toward the sea surface in the entire basin area. These processes weakened aeration of the shelf floor and apparently thinned the upper oxidized layer and the pyrite-accumulating sediment horizon. The conditions apparently approximated those of early diagenesis, as previously described in conjunction with present seafloor deposits (Fig. 1). The position of early diagenetic reworking of seafloor beds, enriched in reactive Fe and OM, along with the development in them of optimal conditions for pyrite-forming aeration led to the increased consumption of OM in these beds. This apparently resulted in an organic carbon minimum in the upper Novoeuxinic horizon. Figure 2a-d shows assumed changes in the pyrite Fe profile with respect to selected seafloor sediments at this geologic moment.

In the transitional interval to the Early Black Sea stage (Hl_{Π}), the increase in total reactive Fe and Fe_{pyr} content have slowed. Total component values showed but minor variations, while these variations, expressed in percentages of total reactive Fe content, may be quite abrupt. The amount of detrital Fe decreased somewhat in the sediments (Fig. 2) and even increased on a number of occasions. Traces of reactive Fe(III) and hydrotroilite generally were absent. In contrast with the residual organic content in Early Black Sea deposits the free H_2S content either remained at its previous level or increased slightly (e.g., from 0.5-1 to 2 mg/liter) [4]. The organic carbon content in the Early Black Sea deposits, as compared with the Late Euxinic, increased on the average from 1-1.5%, to a maximum of 2.5%. This demonstrates differences that often reflect opposing trends of change, associated with the region or part of the shelf [6]. Such organic carbon values apparently do not correspond to the anomalous, very intensive Early Black Sea bioproduktivty process. The organic carbon values in the basin reached a maximum of 17% [5]). However, this shelf area would be expected to display maximum values. our previous explanations apply here.

A great increase in Early Black Sea bioproduktivty and in relative amounts of oxygen-depleted basin waters that reached the shelf led to further reduction in sediment and bottom water aeration. Finally, a stationary depositional and diagenetic regime developed through geological times. In describing it one notes the same associated interdependent processes that determined the early diagenetic alteration trend in sediments of the microzones and in recent shelf floor layers in general. It involved oxidation of the initial organic matter, the total $\text{S}_{\text{H}_2\text{S}}$ content, and Fe(II) by oxygen, formation of assimilated organic matter and, based on it, the total $\text{S}_{\text{H}_2\text{S}}$ and Fe(II) content due to this oxidation.

A sharp increase in the organic content in this photic zone setting resulted in increased consumption of $\text{O}_{2(p-p)}$ and formation of a zone of its optimum concentration in the ore bed, with increased reworking of suspended sediment matter by oxidizing-reducing reactions. Surface reworking of dispersed particles, with accumulation of assimilated organic matter and reactive Fe led to their increased surface activity and accretion. organic-mineral aggregates formed in anaerobic microzones with further localized consumption of $\text{O}_{2(p-p)}$. Sulfate reduction also took place and reduced forms of Fe and S have developed. In final stages of the process aggregate particles of the suspension may apparently change their dispersed state. The accumulation of reducing forms and presence of free H_2S may lead to highly anaerobic conditions in the water and to previously described self-limiting reducing processes. Thus, under conditions of oxygen deficit and excess organic matter the whole complex of these early diagenetic microbiological and chemical processes in the Early Black Sea Stage may have been transferred from seafloor deposits to shelf water layers. In the process, deposits of reducing, "diagenetic" components apparently agree with sedimentary principles and are in conformity with suspension fractionation processes. Detrital iron forms are also involved. However, in contrast with the behavior of reactive iron, their oxidiz-

ing—reducing reconstitution is much slower and restricted to surface alterations. For this reason, the impact of optimum conditions on the conduct of detrital Fe primarily result in the reworking of these forms into organic-mineral aggregates in the fractionation process on and outside the shelf.

At the same time, the hydrodynamic aspects of the shelf prevented prolonged anaerobic conditions. During intensive mixing of water column becomes aerated and the least stable reduced forms became oxidized. The inevitable presence of these two conflicting trends may point to early diagenetic sediment reworking in Early Black Sea times, caused by periodic fluctuations in anaerobic conditions in the water, or extreme conditions of $O_{2(p-p)}$ -deficit with periods of active aeration. Consequently, in Early Black Sea times and more extensive areas, and time interval; under quite different physical conditions, the sediments appear to have been subjected to the same early diagenetic process and rhythmic deposition as recent shelf floor deposits presently are.

Specific characteristics of the physical framework of the basin; the impact of early diagenetic microbiological and chemical processes on suspended matter allow stable sediments to persist the highly variable reducing—oxidizing conditions. This is explained by the free access of oxygen and sulfate to reducing microzone boundaries, in contrast with sediments, unlimited by macrodiffusional stages. These conditions allow multiple recurrence of alternating oxidizing and reducing phases within dispersed particles. Due to their dispersed state, they support such sediment stability. Shelf deposits, as the result, are characterized by threshold conditions in terms of the depth of early diagenetic reworking and the degree of fractionation. Apparently, these very condition explain by the presence of high wave energy conditions and of a constant, intensive counterclockwise circulation, the small organic carbon content in the Early Black Sea shelf sediment as the result of intensive loss of organic matter. The organic matter possessed higher sediment stability in the deep water basin. The same occurs with the excess of reactive Fe, in particular in aggregates of organic matter and insufficiently pyritized particles. This also explains the relative stability of the total reactive Fe and the FeS_2 content in the section of this unity that is attributable to fractionation. Fractionation depends on the proportion of pyrite; the heaviest component in the suspensions and on the basin depth. Thus, depositional conditions in any given part of the basin are essential. These conditions control the distribution trends of organic C and components of the reactive Fe group in the section. They may be studied individually in cores of the Kalamitsk shelf off the Crimea. Most distribution described effects here [6] (Stations 797, 800, 795) are satisfactorily explainable according to the discussed theories by the increased shelf depths during the transgression.

The overwhelming success in explaining early diagenetic processes from the behavior of suspended matter also explains the absence or reduction of admixed quantities of reactive Fe(III) and hydrotroilite in Early Black Sea shelf deposits. These do occur in Late Novoeuxinic deposits (Fig. 2). Apparently, due to repeatedly alternating reducing and oxidizing conditions, aggregation and dispersions, in contrast to sediments, this led to a more intensive, practically comprehensive reworking of the reacting Fe in FeS_2 and nonsulfide forms. These were stable with respect to minor amounts of H_2S . For this reason, H_2S , isolated under anaerobic conditions during the deceleration of sulfate reduction process, was unable to associate with hydrotroilite and may have accumulated and became preserved in significant volumes in the Early Black Sea deposits.

The end of Old Black Sea stage of sediment accumulation is related to the end of the displacement of Novoeuxinic waters and development of stratified conditions. This indicates the presence of bioproductive sea waters, very similar to the present process, involving all biogenic elements that had accumulated in the Novoeuxinic Basin. A correspondingly decreased bioproductivity manifested itself primarily by a sharp reduction in excess organic matter that had created anearobic conditions in shelf waters. At the same time, the organic matter was actively transported into the deep-water basin. For this reason, the organic matter content in sediments in given shelf areas was slightly reduced or remained unchanged (Fig. 2 [6]). Due to establishment of a new hydrologic regime in the upper part of the basin, the reduced influx of Novoeuxinic waters led to reduced influx or stabilization of the reactive Fe content in conjunction with the establishment a new hydrologic regime in the upper part of the basin. This involved formation of an oxidized marine zone in its present form and a sharp reduction in suspended organic matter that led to improved aeration of the shelf and renewal of an early diagenetic process complex, primarily in the upper sediment intervals. Nevertheless, the rather high level of bioproductivity in the Late Holocene basin and hydrogen sulfide contamination of the deep basin at this time may explain the permanent and periodic oxygen deficit that occurred in shelf waters. The early diagenetic process may have taken mostly place under the control of rhythmic sediment redeposition throughout the Late Holocene (Hl_{III}) time interval. In part, it may have also been impacted by diffusional aeration that influenced underlying beds of variable thickness.

During Late Holocene times stable organic matter and reactive Fe concentrated in the sediments. The Fe and S content in the H1_{III} horizon was apparently controlled by the general aeration intensity and interrelationship between regimes. The stable total reactive Fe content is the core of Station 861 (Fig. 2e [6]), reflect relatively stable hydrodynamic conditions and generally reduced sediment aeration in this part of the narrow Bulgarian shelf. Under these conditions, diffusional aeration did not occur and early diagenetic process occurred exclusively in the 10-15-cm-thick mobile surface slope, where the final mineral complex of Fe and S forms corresponds to maximum pyritization reactive Fe (Fig. 1). To a certain extent, this also happened in sediments of Sta. 822 on the Anatolian shelf where similar conditions prevailed (Fig. 2d [6]).

Sediments of Stations 797 and 800 of the wide Kalamitsk shelf are much more distant from the deep basin with a counterclockwise circulation (Figs. 1, 2a,b) [6]. Hydrodynamic conditions in bottom waters have undergone greater fluctuations. In addition to the intensive early diagenetic process in the surface sediment layers that control rhythmic redeposition, for this reason it is presently more likely that episodic aeration involved the maximum 1-1.5-m-thick sediment units. This may have led to partial oxidation of earlier reduced forms and to occasional minor renewal of the diagenetic process in these horizons. In particular, the role of diffusional aeration may be reduced as the result of intensified reduction processes in seafloor layers, caused by increased bioproductivity in the region and changes in hydrological conditions.

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NEW ORE ZONATION DATA FROM THE ATASUIISK Fe – Mn DEPOSITS

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Exploration data from Atasuisk Region deposits provided four examples of ore zonation (West Karazhal, South Klych, Ushkatyn-III, Ushkatyn-I). Along a well-defined trend, Si–Fe–Mn compounds were deposited from hydrothermal sources. They possessed increasing degrees of mobility. Semiconcentric concentration patterns formed in West Karazhal and Ushkatyn-III deposits, while Mn-ore beds evolved in South Klych, associated with hematite ore veins in the initial zone. The Ushkatyn-I deposits represented a unique Fe–Mn ore zone, absent from other locations.

We have previously discussed lateral zonality in the Atasuisk region Fe–Mn deposits. In addition to describing directional trends in the alternating ore mineral zones [9, 10], we also corrected previous assumptions [6, 11] regarding the nature of zonation. In particular, it is now shown that the West Karazhal ore zones are not linear but semiconcentric (Figs. 1, 2). The incomplete state of exploration in the West Karazhal deposits at that time did not produce many important and interesting details. Such were unavailable until 1984–85 when exploration work was completed and the ore deposit completely outlined.

Over 98% of the Fe and Mn ores in West Karazhal occur in a single, complex deposit. Unlike other deposits of the region (Ushkatyn-III, Zhomart, etc.), during its formation the ore bodies were not interlayered with large portions of nonore matter. The great depth of the western half of the ore deposits prevented erosion of the entire facies profile of the ore-bearing deposits and complete erosional dissection of the ore body in extensive areas. This deposit therefore is best suited for the study of ore zonation.

In horizontal projection, the deposit (Fig. 1) is a 5.5 km long and, on the average, 0.7–0.8-km-wide elongated lens [2, 9, 10]. Small- and medium-scale folding, parallel with the deposit's long axis, generally occurs with southward dip of the beds (Fig. 2). The southward increasing thickness of ore-bearing deposits, noted by numerous workers, was taken as indication of the basin's southward dip at the time of the ore deposition [9].

Crests of the longitudinal folds plunge westward at 10–15°. This displaced the ore body to a depth of 1200–1500 m at its west end, while allowing its erosional removal on the eastern ore margin.

From its northernmost outcrop in the surface, as the result of its south dip the depth of the deposit increased gradually southward. This erosional sculpted, ore-free surface outcrop unit correlates with the ore-bearing horizon.

In our previous publications the north–south sequence of ore mineral zones that consist of Fe-jasper, magnetite, hematite, and Mn ores represented a general trend. Distribution of the ore types along profiles, drawn across the deposits and the composition of the zones indicates that conditions are much more complex. Along lines of drillholes that parallel the strike direction of the deposits, the magnetite ore alternates with hematite or Mn-ores. The fringe Mn-ore zones of simple or complex composition occur in the middle portion of the deposit, in the foot and hanging walls of the iron ore body. The complex ore type includes alternation with hematite layers. Only near the southern wedgeout zone of the deposit do Mn ores thicken (Fig. 2). In profiles of the western and eastern areas deposits of the manganese ore fringe zone accompany the hanging and footwalls of the ore deposit along the entire profile, all the way to the northern wedgeout.

In addition to magnetite silicate (chlorite, ferrostilpnomelane) and carbonate minerals (siderite, Fe-calcite), iron minerals in certain areas include a maximum 30% of the iron ores. In contrast with the ferrous iron zone, this zone may be termed the ferric iron zone. Hematite metals almost always contain single dispersed, idiomorphic magnetite crystals [11], either as magnetite nests that consist of an aggregate of optically almost identical, minute crystals. While the relative amount of such magnetite is small, its theoretical significance is great as the Ge-accumulator in the ores [8].

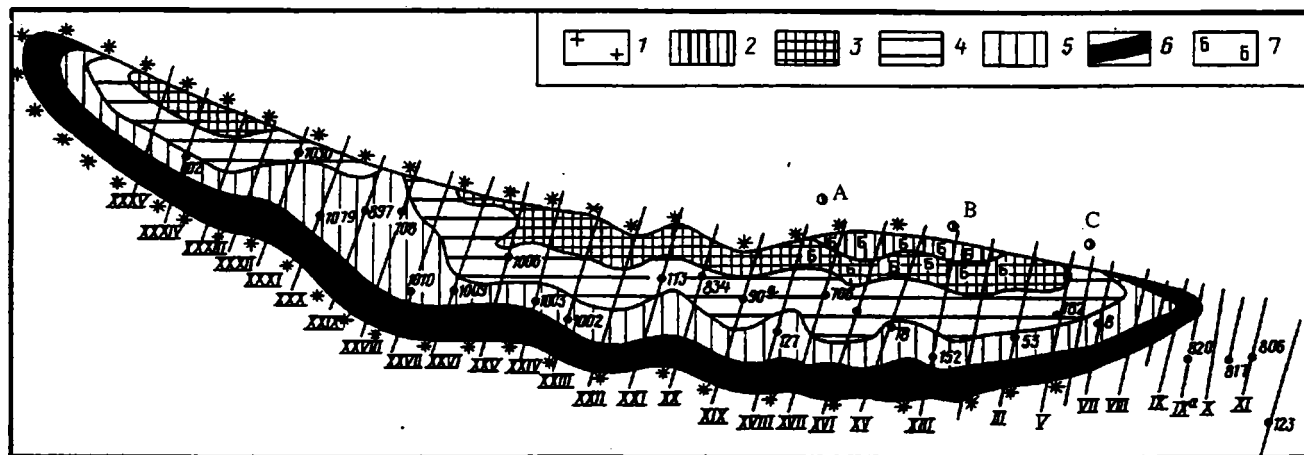


Fig. 1. Zonation of West Karazhal deposits: 1) Mn-Fe-Si-carbonate rocks; 2) Fe-jasper; 3-6) ores (3 - magnetite; 4 - magnetite-hematite; 5 - hematite; 6 - Mn-ores); 7) barite mineralization; A, B, C) mine shafts (A - main; B - ventilation shaft; C - eastern). Roman numerals mark exploration profiles.

Data from all deposits on the complex distribution pattern of ore mineral types at first glance may raise doubts about our previous assumption on ore zones. However, insightful interpretation resolves the apparent contradictions. Ore deposits of the Western Karahhal contain individual thin beds, totaling 45-50 m and more in cumulative thickness. These deposits formed over an extended period of time in the course of changing sedimentary conditions that were responsible for the layering. Adjacent layers differ mostly in quantitative relationships between the enclosed ore and nonore matter. Nonore matter included nonore grains of quartz, calcite and minor clay mineral matter (illite). These components form the enclosing rocks beyond the limits of the ore body and represented the background for deposition in the entire ore region. Dominant current theories that we endorse, assume that in the Atasuis deposit hydrothermal solutions were the source of ore matter. They reached the basin floor through tectonically fractured zones. ores formed through reaction with sea water. Each ore-bearing bed thus formed by the alternation of two different components; the hydrothermal ore and the non-ore matter of terrigenous, chemical or ologenic origin. Hydrothermal components dominated near hydrothermal spring locations; while non-ore constituents were predominant at maximum distances from the hydrothermal discharge source. Here the ore content declined to a minimum. Accordingly, hydrotherm centers coincide with ores that contain no or only few, small ore-free beds. They are located in the northern half of the ore belt and along its northern boundary. At the southern boundary of the deposit, at maximum distances from hydrothermal springs the Mn ores occur in frequently alternating non-ore rocks, mineralized rocks, and ore beds. The role of ore-free layers significantly increases.

The hydrothermal solutions were transported downdip on the seafloor and have deposited ore beds. ore participation in the beds eventually ceased completely. The bed's composition thus depended directly on the intensity of the hydrothermal process. With intensification of this process, the distance traveled by the solution increased. It dwindled when emissions declined. This determined also the downdip distance of specific ore beds.

Downdip changes in the composition of an individual ore bed, coincided strictly with ore zonation: jasper → ferrous/ferric Fe-minerals → Fe-oxides minerals → Mn-oxides. As the hydrothermal process intensity increased, so did the mineral zone boundaries shift downdip. This generated ferrous iron zones that covered ferric iron deposits, and ferric oxide mineralization, directly overlying Mn-ores, and so forth. Reduction in process intensity resulted in reverse zone boundary shifts downdip and covered hematitic beds with Mn-ores and magnetite layers with hematite beds, etc (Fig. 3).

A maximum of hydrothermal impact in the middle part of the deposit resulted in maximum shift in mineral zone boundaries downdip. This resulted in the greatest southward advance of Fe and Mn ores.

In the next ore development stage, the boundaries of the Fe and Mn ores and of overlying iron ores retreated laterally from the hanging wall of the Mn ores. Cessation of hydrothermal activity was followed by complete burial of the ore deposits by Si-carbonate rocks that covered the ores.

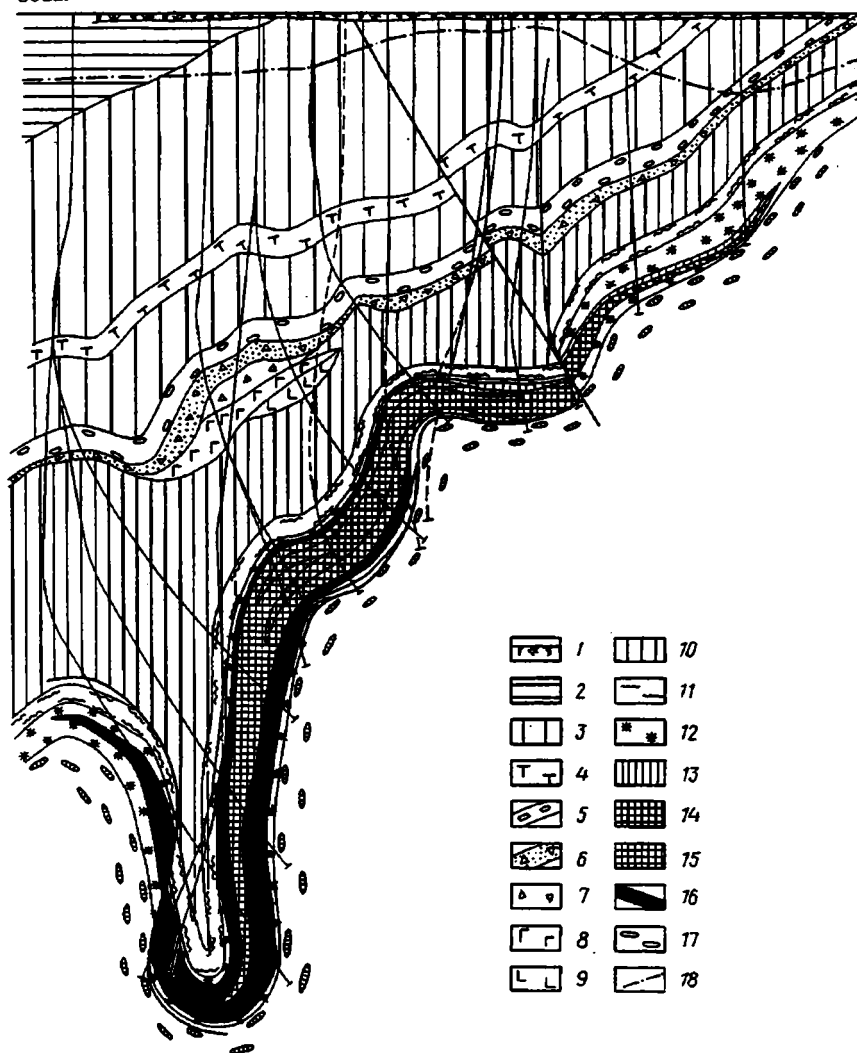


Fig. 2. Geological cross section along profile XX, West Karazhal Deposit: 1) Quaternary deposits; loams and sandy loams; 2) clayey-carbonate-Si rocks; 3) ash-gray limestones; 4) tuffites; 5) nodular limestones (C_1t_2a); 6) depositional breccias, aleurolites; 7) brecciated; 8) with gypsum mineralization; 9) massive and amygdaloidal diabases; 10) clayey-siliceous-limey rocks of flysch facies; 11) nodular, layered limestones ($C_1t_1a_1$); 12) red limestones ($D_3fm_2b_3$); 13-16) ores (13 - Fe-rich, of balanced jasper-hematite content; 14 - magnetitic, Fe-bearing, with carbonate and Fe-silicate admixture; 15 - hematite iron content; 16 - Mn-content); 17) Si-carbonate rocks with silica lenses ($D_3fm_2b_2$); 18) lower boundary of weathering horizon.

The more than 1.5-km-wide iron jasper zone occurs in the center of the Western Karazhal ore zones, in the area of hydrothermal spring orifices. In such a broad area, one would not expect all springs to produce equal volumes of hydrotherms. In each cross profile details of ore zonation differ, resulting in areal heterogeneity of the ores (Fig. 3).

A theoretical chemical interpretation of the Atasuisk Fe-Mn ore deposit zones would be important. As known, Fe and Mn enter solution only in bivalent state and both metals migrated as bivalent species in the solutions. Judging by the color and the geochemical characteristics of the ore-bearing rocks, it appears that oxidizing conditions prevailed in the depositional basin during ore formation. As ascending hydrotherms came in contact with marine waters of the basin, Fe and Mn consequently became oxidized.

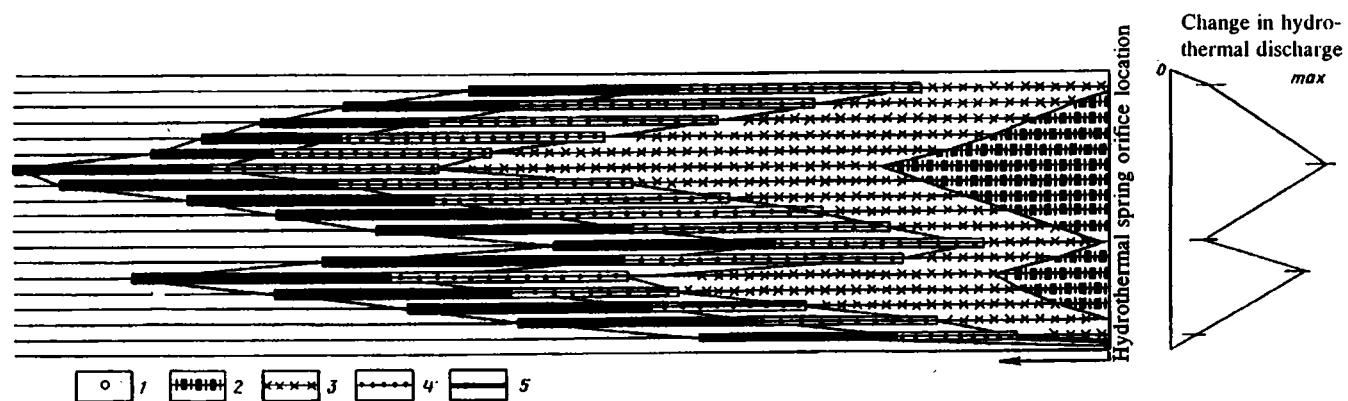


Fig. 3. Generalized pattern of main ore body zones, West Karazhal. (Due to changing hydrotherm discharge locations, ore zones shifted with changing boundaries): 1) hydrotherm discharge source; 2) Fe-jaspers; 3) ferrous and ferric oxide ores; 4) Fe-oxide ores; 5) Mn-ores. Arrows: discharge direction.

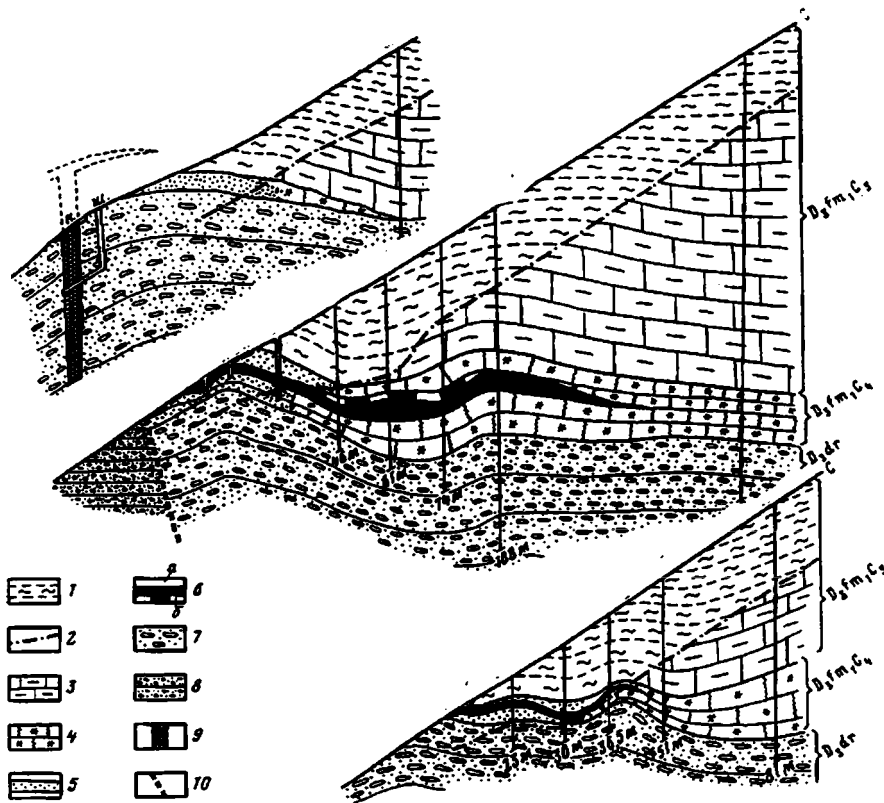


Fig. 4. Geological cross sections of South Klych deposits: 1) loose, clay-like weathering products of carbonate rocks; 2) lower boundary of weathering horizon; 3) clayey-silica-carbonate rocks of flysch-type composition; 4) ore-bearing nodular-layered red limestones; 5) ore-bearing polymict sandstones that replace limestone facies; 6) Mn-ores (a - balanced; b - initially balanced); 7-8) conglomerates (7 - with sandstone layers; 8 - with schistosity); 9 - jasper-hematite ore veins; 10 - fault dislocations.

The diverse nature of salty sea waters and hydrotherms caused quick coagulation of Si from the hydrotherms and its accumulation as jasper near the hydrothermal spring orifices. The presence of nodules and disseminated hematite pigmentation in the jasper indicates partial iron oxide coagulation and its incorporation into silica. Iron compound oxidation did not occur simultaneously in Si-free hydrotherms outside the jasper zone; not throughout the entire volume of the solutions. Nearer the orifices where hydrothermal spring activity, bearing bivalent iron and manganese, continued uninterrupted, only partial oxidation and hydrolysis of iron compounds took place. As the result, a mixture of ferrous and ferric hydroxides precipitated in the sediments. Diagenesis resulted in magnetite ore formation in such deposits, to varying degrees associated with ferrous silicate and carbonate minerals.

Mn, a strong oxidizer, led to oxidation of ferrous iron and itself remained of lower valence. It was transported in the hydrotherm flux. Solutions down-dip traveled over the seafloor slope and in muddy pore waters, within the mass of nonlithified, earlier deposited sediments. Later, as contact with oxidized marine waters weakened, this resulted in the more prolonged preservation and greater migration distances of certain volumes of ferrous iron. Ferrous iron developed nodules and idiomorphic magnetite crystals in cryptocrystalline hematite ores during subsequent diagenetic and katagenetic processes.

As oxidation impacted the hydrothermal solutions that flowed down-dip, precipitation and settling of ferrous-ferric iron compounds alternated with the settling, pure hydroxide compounds. Subsequently, the Mn compounds became oxidized and lost their mobility. This is why the Mn ore zone became spatially separated from the hydrothermal spring locations.

Localized, "anomalous" Mn compounds, in "anomalous combination with ferrous oxide occurred in muddy pore waters of the sedimentation zone. Under these conditions Mn ores included the Fe-Mn mineral jacobsite.

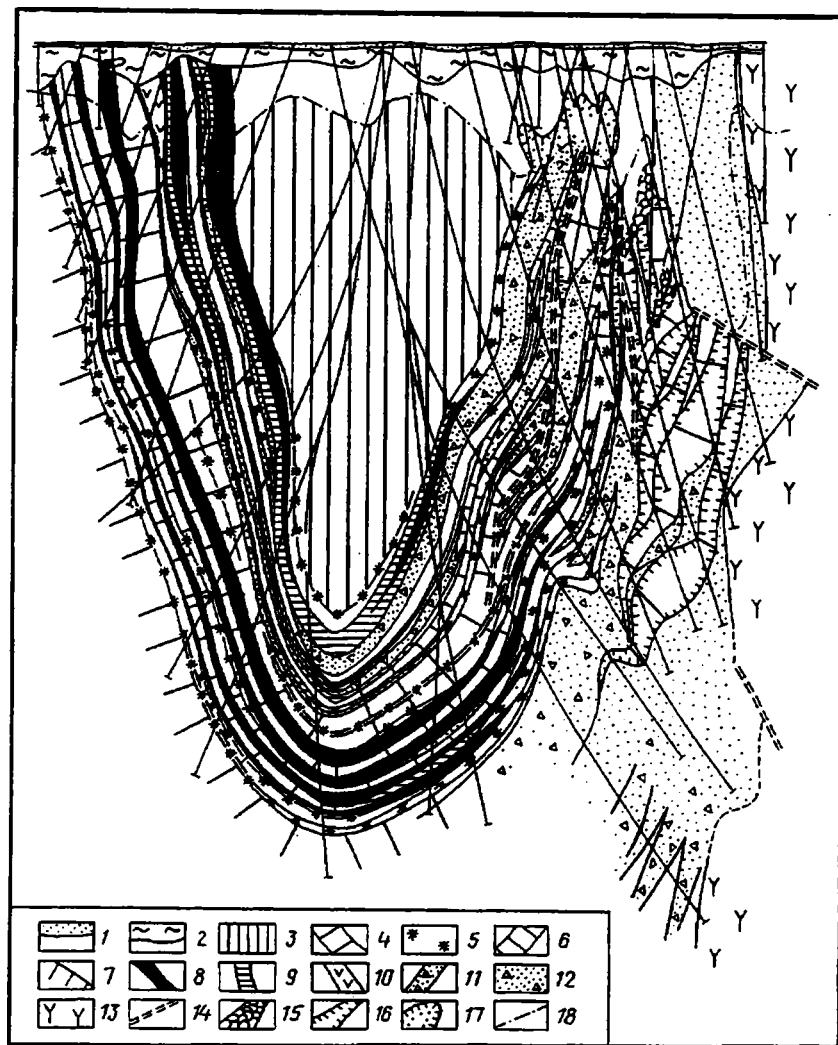


Fig. 5. Geological cross section along Profile V-V, Ushkatyn-III Deposit: 1) Quaternary deposits, sands and sandy loams; 2) Paleogene clays; 3-7) limestones (3 - detrital; 4 - biogenic-detrital; 5 - red; 6 - reef limestones; 7 - lenticular siliceous and nodular-bedded); 8 - Mn-ore bodies; 9 - Fe-ore bodies; 10 - diabase porphyries; 11 - sediment breccias, aleurolites; 12 - sandstones, aleurolites, sediment breccias of the Dairinsk Formation; 13 - trachy-rhyolite porphyries; 14 - tectonic dislocations; 15 - crushed zones; 16 - barite-lead sulfide ores; 17 - barite-lead oxide ores; 18 - lower boundary of weathering horizon.

The consistent distribution pattern is disturbed by the fact that ferric oxides pigment the jasper zone minerals around the hydrotherm orifices, while ferrous ore facies occur at some distances. In the area around the orifices one should expect only ferrous iron compounds. We turn to another model [12] to explain this contradiction. Skripchenko assumed that the ascending hydrothermal spring fountains delivered part of the solutions high into the upper water layers. Iron oxidation, iron oxide hydrolysis, and coagulation took place in such zones. Subsequently, the coagulates settled slowly on the seafloor. During the study of certain Atasuis deposits, Kayupova [7] also concluded that part of the iron silicas and hydroxide gels occurred in suspension in sea waters. Their aggregates later settled jointly on the seafloor. This is why inclusions of silica-hematite nodules occur in various rocks and ores.

It may well be assumed that the jasper zone developed only in those zones of upward oozing hydrotherms where under great pressure they became converted into ascending and gushing underwater geyser-springs. This explains their locations along the 1.5-km profile where the ore field's length exceeds 5.5 km (Fig. 1).

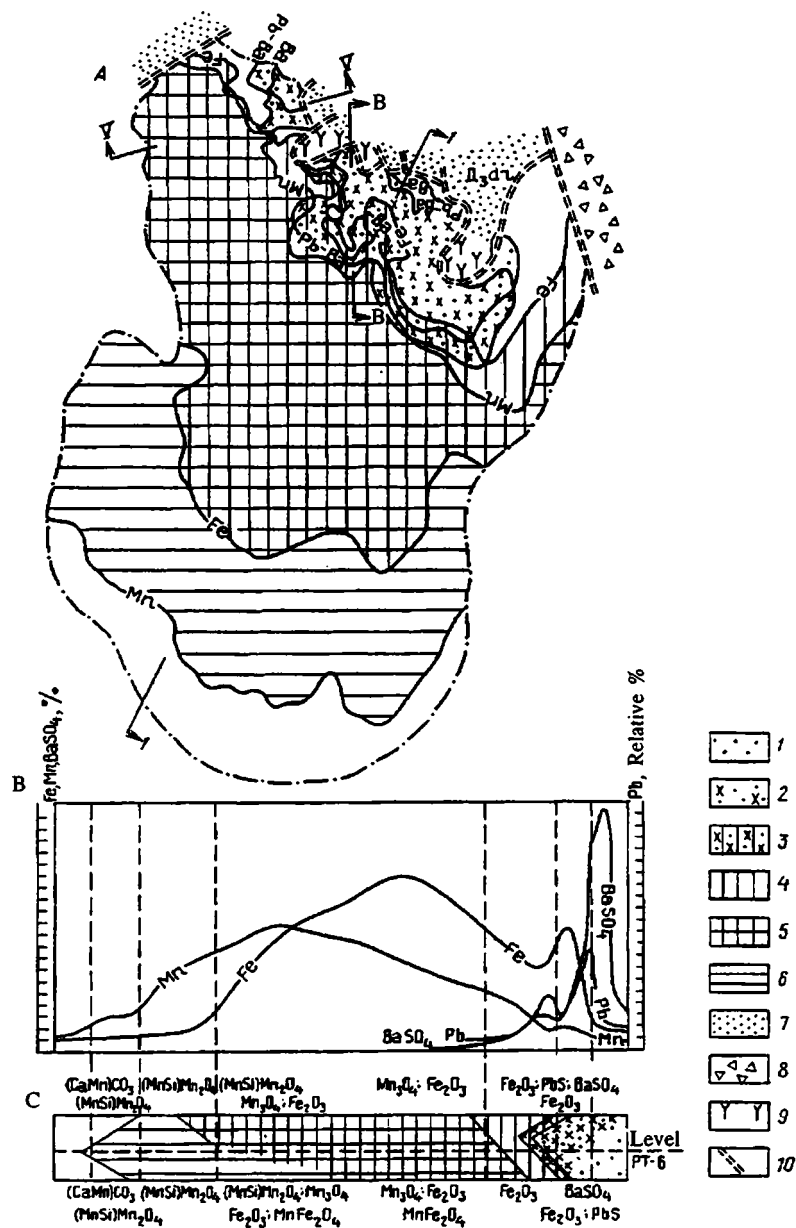


Fig. 6. overall aspects of Ushkatyn Ore Deposit III (A – surface pattern; B – composition curves; C – generalized profile): 1-6-zones (1 – mostly barite ores; 2 – barite-lead ores; 3 – hematite ores with barite-lead mineralization, 4 – hematite ores; 5 – alternating hematite and barite-hausmannite Mn ores; 6 – Mn ores); 7 – aleurolites; 8 – sediment breccias; 9 – felsite porphyries; 10 – tectonic dislocations.

In hydrothermal spring areas, the zonal sequence may be shortened. Hydrotherm interaction with sea water and consequent oxidation and precipitation of part of the iron compounds may occur along fractures where ascending hydrotherms encountered sediments beneath the ore beds. Jasper-iron ore veins formed here. Under such conditions, iron-free solutions may have poured over the seafloor, forming only Mn ores. The small South Klych ore deposit provides a good example of a combination of Mn ore layers with jasper hematite veins in the subore beds (Fig. 4).

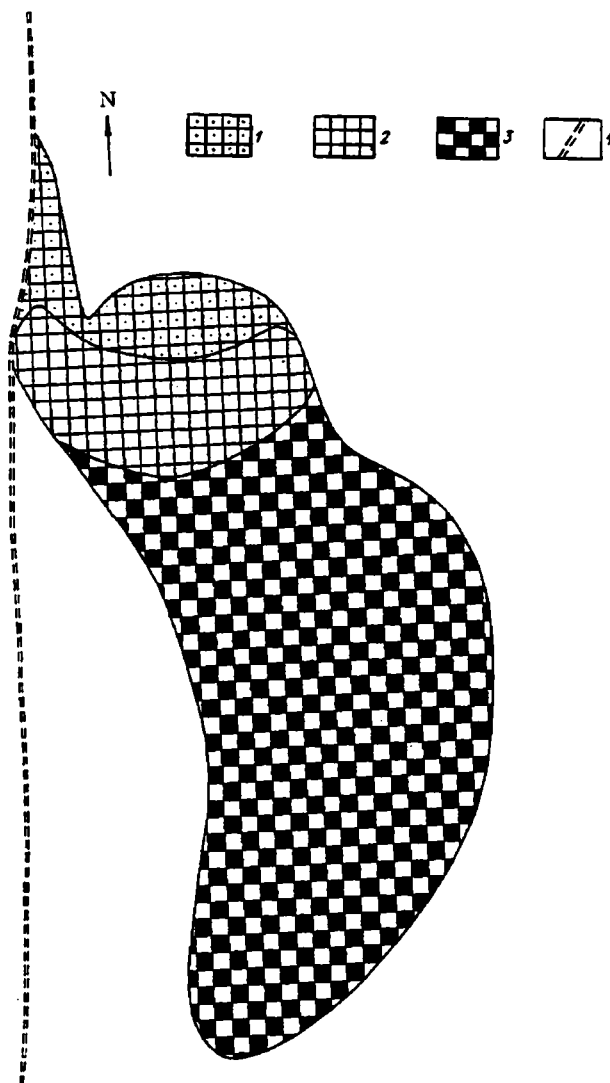


Fig. 7. Zones in Fe – Mn deposits, Ushkatyn-I Deposit: 1) hematite ores with dispersed idiomorphic magnetite grains; 2) hematite ores; 3) Fe – Mn (hematite – braunite – jacobsonite) ores; 4) tectonic faults.

THE ORE-FORMING PROCESS AND ZONES IN THE USHKATYN-III DEPOSIT

Just as in the Western Karazhal deposit, in the Ushkatyn-III deposit the Fe – Mn ores were laid down in the same stratigraphic interval [4, 5]. However, instead of a single deposit, there are 14 ore beds (Fig. 5), separated by massive, gray, finely detrital limestones with aleurolitic and psammitic detrital grain size. Absence of layering indicates that they formed very fast and in a single interval. They appear as the result of suspension currents that, emanating from shallow water zones, periodically invaded seafloor depressions. As in the case of the Karazhal Deposit, the seafloor was slowly filled by products of hydrothermal activity. Mud deposition concurrently also took place in the basin. Hydrotherms throughout a time period penetrated upward through the limestone detritus and formed the ore muds of the next bed. In addition to sufficiently large suspension currents that cut up the ore beds, small layers within the complex detrital limestone beds indicate the short time interval that was associated with ore bed formation. Under these conditions the ore body zones were not as sharply defined Karazhal. Clogging by introduced limestone detritus of hydrothermal passageways had interrupted various stages of the ore-forming process. Resumption of hydrotherm seepage led to a gradual increase in hydrothermal discharge, as detrital limestone "plugs" that sealed solution passageways gradually opened up through this

"cleaning" process. In each ore bed a very complex alternation of Mn-ores and hematite layers takes place. It was hard to establish any component-distribution patterns in a given bed. Only the dominance Mn-oxide beds, indicative of mostly moderate volumes of hydrothermal flow due to frequent cessation of ore formation, was noted. In summarizing all 14 ore bodies and quantitatively averaging mineral content in each profile throughout the entire ore body, Altukhov [1] compiled a generalized chart of lateral zonation (Fig. 6), very similar to that of the Western Karazhal map. The one exception: the ferrous iron ore zone in the Ushkatyn-III ore deposit had been sharply reduced. To a large extent it is unrecognizable.

We believe that, in contrast with the Karazhal area, this was caused by the higher oxygen saturation of sea waters in the Ushkatynsk area. The basin was shallower and, as the result iron compound oxidation more thorough even in the immediate vicinity of hydrothermal orifices.

COMPARISONS OF COMPOSITION AND ZONATION, USHKATYN-I DEPOSIT

In contrast with the other discussed ore deposits, Ushkatyn-I [3] formed in very small seafloor depressions in which the routes of hydrothermal solutions were defined by depression boundaries (Fig. 7). Thus, Fe and Mn separation occurred only along the initial stretch of that route. At a certain downroute distance, solutions that contained the two metals slowed their movement in the depression. Fe- and Mn-hydroxides precipitated jointly and formed Fe-Mn ores that contain large volumes of jacobsonite. This is how the single, bizonal ore deposit developed. The northern, smaller deposit includes hematite ores, the larger southern Fe-Mn ores with dominant jacobsonite and hematite mineralization. Ferrous iron ore zones did not form in the Ushkatyn-I deposits. The high degree of the deposit's erosional dissection prevented clearcut conclusions. It is not known whether this zone, along with the jasper zone had been eliminated by erosion, or, similarly to the Ushkatyn-III deposits never formed, in the first place.

* * *

Four types of zonation (West Karazhal, South Klych, Ushkatyn-III, and Ushkatyn-I) were discussed. Similar zonality occurs in the western and eastern Karazhal area [9]. Despite their variety, the zone categories have the same development sequence. Starting from a hydrothermal source, it includes compounds with gradually increasing mobility (in our case, silica Fe Mn). The process mechanism was highly complex. In the Zhairmsk deposits, involving a level seafloor paleorelief, the hydrotherms spread in every direction from the source spring locations, forming semiconcentric zonation. The hydrotherms were able to flow only downward, and laterally from the spring locations, not effecting seafloor areas at higher elevations.

Due to the weak hydrothermal pressure, mixing between hydrothermal and H₂S-bearing marine waters did take place in underlying feeder zone fractures in South Klych deposits. Mn-ore layers formed, associated in the initial stage with hematite ore veins.

Specialized mineral zones (Fe-Mn ores) formed where hydrotherms were unable to escape from small depressions on the basin floor (Ushkatyn-I). These zones are unknown from the other ore deposits.

In all likelihood, all variations in zone types have not been exhausted by those, discussed in the present paper. Further studies of Atasuisk deposits certainly will provide new material in important and interesting investigations of the hydrothermal-sedimentary ore genetic processes.

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LITHOGENESIS AND OIL POTENTIAL OF JURASSIC TERRIGENOUS DEPOSITS OF THE MIDDLE-LATITUDE OB RIVER REGION

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UDC 552.14:552.578.2

The lithologic, mineralogical, and geochemical features of Jurassic terrigenous deposits of the Krasnoleninskii group of oil fields of Western Siberia are characterized. It is shown that the degree of their regional changes corresponds to the protocatagenesis-mesocatagenesis interval PC_2 - MC_1 and only to the start of the main phase of oil generation. At the same time pronounced fluctuations of the paleo-temperature indices related to the repeated intrusion of hydrothermal fluids were noted. It was established that the formation of secondary oil reservoirs in Jurassic deposits is a multiphase metasomatic process, including tectono-geodynamic and hydrothermal alteration and oil saturation accompanied by various "near-oil" alterations of the enclosing strata and formation of a system of geophysical and geochemical anomalies.

Interest in the problem of the "geologic similarity of oil fields and fluid-producing ore deposits" [13, 15] arose in recent years, since features of the similarity of hydrocarbon potential and hydrothermal-deposit potential markedly increase with depth. The fields discovered in the Dnepr-Donetsk, Caspian, Anadarko, Perm, and other petroliferous basins at depths greater than 5 km, as a rule, are confined to massive, often columnar reservoirs (typical examples: Tengis, Karachanank, Gomes, Yablunovskoe, and other oil and gas-condensate fields in deep-seated carbonate and terrigenous complexes), and shallower reservoirs are often related here to various vein (not only to intersecting tectonic barrier but also more often stratiform, conformable) as well as stockwork and pocket forms. Their distinctive features include [8-11]: 1) intense manifestation of stylolitized injection dislocations and various open jointing; 2) stable paragenesis of naphthids [hydrocarbon gases, condensates, and their natural derivatives] and various hydrothermal mineralization; 3) occurrence of hydrologic inversion and other signs of an unsteady geothermohydrodynamic regime. All this makes it possible to relate the basic prospects of deep horizons of petroliferous basins to morphologically diverse (vein, stockwork, etc.) hypogene-lithologic-epigenetic traps. This is the only genetic type of traps (reservoirs) whose significance does not decrease but increases with depth, which is accompanied by an expansion of the range of rocks playing the role of substrate of secondary oil and gas reservoirs [9, 11]. Thus, a study of the regularities of their formation and the development of criteria for predicting commercial hydrocarbon accumulations related to them acquires importance as one of the main directions of present-day oil and gas lithology. Of primary interest from this standpoint are reservoirs in traps of the given type occurring at comparatively small depths. Such objects include the Krasnoleninskii arch and its frameworks in the western part of the middle-latitude Ob River region (MO). The Jurassic deposits of this region in general were judged to play a significant role in a study of the regularities of the oil and gas potential of traps and reservoirs of a nontraditional type. This pertains mainly to the Bazhenovo suite (works of F. G. Gurari, I. I. Nesterov, A. É. Kontorovich, I. I. Ushatinskii, V. I. Belkin, R. I. Medvedskii, T. T. Klubova, B. A. Lebedev, et al.). A further study of the regularities of the oil potential of the Bazhenovo suite and Jurassic terrigenous polyfacies deposits underlying this unique producing complex (and at the same time a regional hydrophobic barrier) enabled V. I. Belkin, R. M. Bembel', R. I. Medvedskii, et al. to establish the leading role of hydrothermal processes in the formation of the oil potential of the Jurassic complexes. Thus, there are all grounds to regard the MO and especially the Krasnoleninskii arch (with the grabens framing it) as a unique test area for working out a method of predicting, prospecting, exploring, and developing fields of the given type. For this a sufficiently complete study of the regularities of their formation, which is a complex multiphase process with the participation of a number of lithogenetic factors, is first of all needed.

V. I. Belkin's deep and diverse investigations made a great contribution to knowledge of the regularities of the oil potential of Jurassic deposits of Western Siberia. He understood the need for the most complete possible lithogenetic substantiation of the "hydrothermal vein" concept. On his initiative lithologists experienced in studying lithogenetic

factors of hydrocarbon potential were enlisted to study the given problem. In particular, one of the authors of this article, having experience in studying the lithogenesis of deep-seated complexes of aulacogen basins, precisely on the invitation of V. I. Belkin has since 1987 investigated the composition and regularities of formation of Jurassic and Paleozoic reservoirs of the MO.

A number of essential mineralogical features of the reservoir rocks of the Tala field were characterized in the recent publication of M. Yu. Zubkov et al. [5].* Our independent investigations (with the use of infrared spectroscopy, x-ray diffraction analysis, scanning electron microscopy) also indicate the wide development of various generations of kaolinite, dickite, quartz, ankerite, albite, adularia, and other minerals in the secondary pore space of the reservoir metasomatites of the Tala and other fields. However, the presence of the indicated minerals per se cannot be considered unambiguous proof of superposed hydrothermal processes, since secondary quartz, perfect kaolinite, dickite, and authigenic feldspars form also as a result of catagenesis. It is necessary to examine the entire set of lithogenetic features and new formations (including the entire joint system) with the use of paleogeothermal and geochemical indices. The purpose of the present work is to give the most complete and objective characterization possible of the complex picture of lithogenesis with an evaluation of the "contribution" of various lithogenetic factors to the formation of oil fields of the Jurassic terrigenous zone of the MO.

MAIN LITHOLOGIC AND FORMATION CHARACTERISTICS OF JURASSIC DEPOSITS

The Jurassic deposits of the MO containing the Sherkaly, Tyumen, Abalak (Georgievka, Vasyugan), and Bazhenovo suites, which accumulated under subtropical humid climate conditions [3], in a formation respect are a clear example of the relation between lithologic features and the paleorelief and geodynamic regime of sedimentation. The Sherkaly suite occurring on different-age or Triassic basement rocks (thickness up to 140 m), differing from the overlying deposits by the predominance of continental-alluvial coarse inequigranular clastic rocks, is confined to systems of paleochannels of ephemeral and river streams. The start of Jurassic sedimentation compared with subsequent development is characterized by a more active and diverse (combination of predominant compression with zonal extension) geodynamic regime. Therefore, the system of grabens forming in Sherkaly time (the occurrence of posthumous rifting) controlled these streams. Here the erosion factor along with the geodynamic played an essential role in the formation of the grabenlike trough-valleys. Such a lithogeodynamic [11] approach makes it possible to eliminate the contradiction between the existing notions about the nature of the zone of distribution of the Jurassic basal continental clastic deposits, which some investigators (A. G. Mukher, G. S. Yasovich, et al.) related to paleochannels and others (V. I. Belkin, O. M. Garipov, et al.) to grabens.

The accumulation of the proluvial-alluvial coarse-fragmental inequigranular Sherkaly deposits compensated the erosion-tectonic paleorelief, and subsequent Jurassic sedimentation had a typical "platform" character. The vertical formation series, including the proluvial-alluvial terrigenous coarse-fragmental molassoid, coal-bearing paralic, terrigenous lagoonal-marine, domanikoid [oil shale-like] marine formations, is characterized by regular structural and mineralogical changes (decrease of the maximum and median sizes, increase of the degree of sorting of clastic material, and increase of the role of pelitomorphous rocks, carbonate content, silicification, and organic matter). Diagenesis and catagenesis act in accord with this formation-controlled tendency, mainly emphasizing and intensifying those petrophysical, mineralogical, and geochemical properties of the rocks which formed or began to emerge in sedimentogenesis. Against the background of these autogenetic [18], i.e., regular evolutionary, changes appear quite nonuniform allogenic [18], i.e., superposed, transformations with various manifestations of decompression. However, the selectivity of these transformations is determined to a greater extent by lithogenetically determined mineralogical, geochemical, and petrophysical properties of the rocks.

Despite the considerable role of superposed processes within the interblock dynamically stressed zones (DSZs) [1], the primary structural, textural, and material characteristics of the rocks, as a rule, are preserved to a degree sufficient for detecting facies and genetic types of deposits. In accordance with the position in the aforementioned formation series, the

*For incomprehensible reasons any references to the widely known works of V. I. Belkin, R. I. Medvedskii, R. M. Bembel', et al. on the given problem are absent in it.

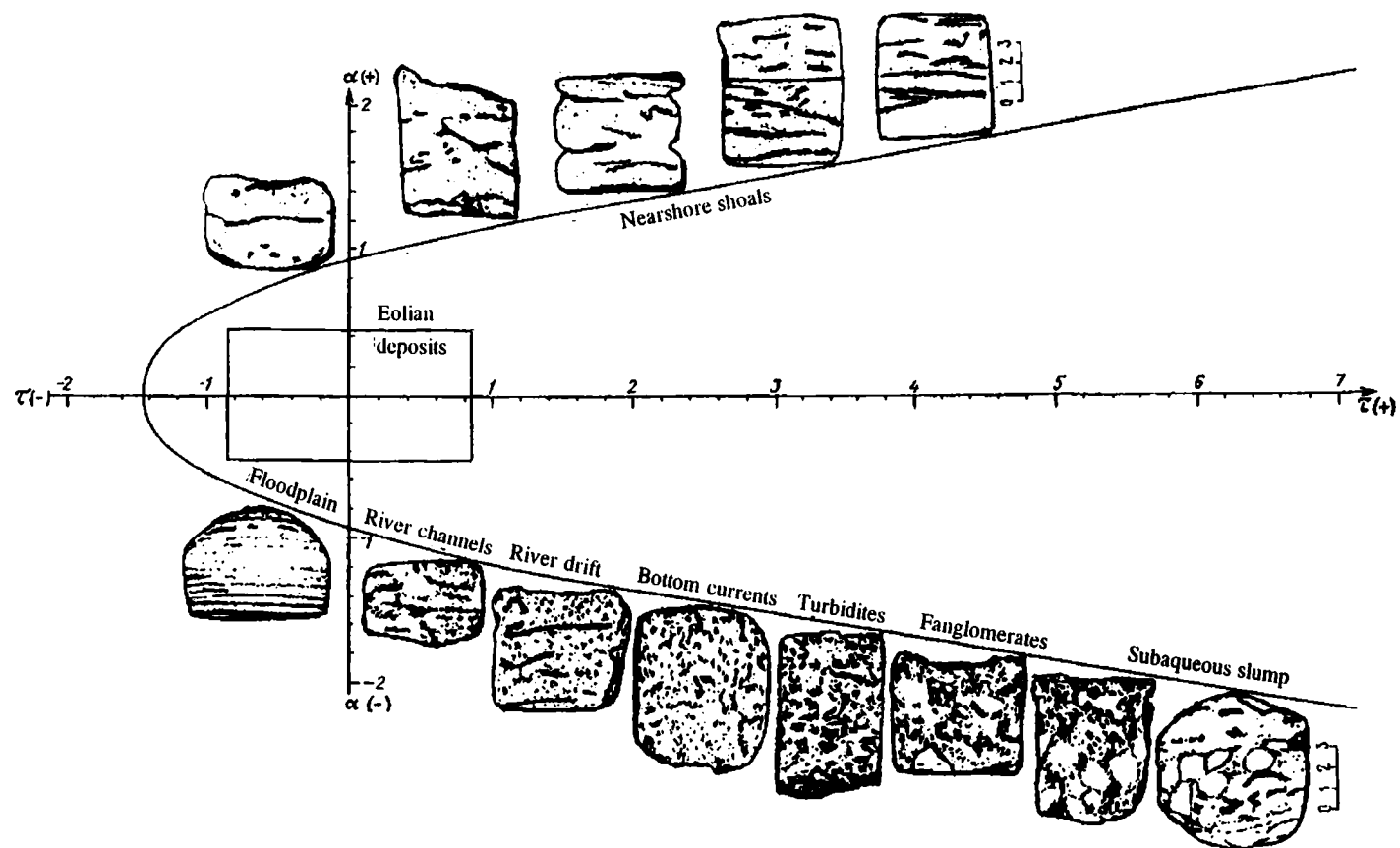


Fig. 1. Interrelation between structural (skewness and kurtosis indices of size distribution) and textural features of the main facies types of clastic rocks of the Sherkaly and Tyumen suites (position of typical specimens on Rozhkov's diagram).

Jurassic terrigenous deposits accumulated in polyfacies, primarily continental and continental-transition (proluvial, piedmont-alluvial, alluvial, subaerial-deltaic, lacustrine—paludal—lagoonal) conditions. With their accumulation the tectono-geodynamically determined energetics of denudation processes decreased (the presence of the coarsest clastic deposits in the basal reservoir formations Yu₁₀₋₁₁), whereas the energetics of the sedimentation environment and, accordingly, the degree of hydrodynamic reworking of the sediment material, conversely, increased (an increase of the degree of sorting and other structural and mineralogical changes up the section). In connection with this, distinct differentiation of the clastic rocks is observed in the fields of G. F. Rozhkov's "dynamogenetic" diagram (Fig. 1). According to this, not only regular changes in textural features but also substantial differences in the intensity of diagenetic mineralization and degree of catagenetic consolidation are observed downward along the parabola. The first reaches a maximum in the upper branch of the parabola (beach-bar sandstones, nearshore shallow-water sand and silt deposits with carbonate cementation). The second is manifested maximally in proluvial and alluvial coarse-fragmental arenaceous and unsorted argillaceous clastic deposits.

MAIN FEATURES OF CATAGENETIC ZONATION

According to existing notions [6] based on determinations of the reflectance of vitrinite microinclusions (to a considerable extent from fluid-permeable clastic rocks), catagenesis of the bulk of Jurassic deposits of the MO reaches mesocatagenesis gradation MC₂(G [gas coal]), and "in individual areas (Krasnoleninskii arch etc.) the organic matter is transformed to the transitional G-MC₂ to F [fat coal]-MC₃ gradation" [6, p. 117]. This corresponds to paleotemperatures of regional heating (165-190°C), whereas the present temperatures at depths of 2700-2900 m vary from 80 to 120°C. However, if we base ourselves on the data on coal interlayers and lenses as well as on spores from dense rocks (clays, siltstones, and sandstones with metahalloysite, imperfect monoclinic kaolinite, glauconite, leptochlorites, etc.), we obtain a substantially different picture. Coals from the Jurassic terrigenous deposits of the MO are presented by grades B3 [brown coal less than 30% moisture content]-C [cannel] (yield of volatiles 38-54%, carbon content 68-80%, etc.). The color index of microphytofossils from clays and dense rocks without signs of superposed hydrothermal reworking is in the range from 3 to 4 scale units [16]. With respect to these indices, in accordance with the generally adopted scale of catagenesis the investigated complex is confined to the range of stages PC₂-MC₁, which corresponds to transition from proto- to mesocatagenesis and only to the start of the main stage of oil generation. Thus, the paleotemperatures of regional heating of the deposits, including the Tyumen and Sherkaly suites, was within 80-120°C, i.e., did not exceed the present-day temperatures. Substantially different paleotemperature indices were established in the arenaceous—coarse fragmental rocks with high reservoir properties (including porosity and fracturing) and secondary mineralization (dickite, triclinic kaolinite, secondary quartz, ankerite, albite, adularia, etc.). Microphytofossils from such rocks markedly darken, corresponding in color indices to gradations MC₅-AC₁ and higher (end of mesocatagenesis—apocatagenesis), which indicates their heating above 220-250°C. This agrees well with various mineralogical and barogeochemical paleotemperature indices. Thus, the "kaolinite—dickite" transition temperature according to the experimental data corresponds to 230-260°C [17]. The formation of K-feldspars (adularia, orthoclase), characteristic for a number of the investigated secondary reservoirs, is related to the temperature range 250-360°C [7]. The temperature range of homogenization of gas—liquid inclusions from authigenic ankerite and quartz is 120-280°C (the oxygen isotope data in quartz—ankerite paragenetic associations give close paleotemperatures).

LITHOPHYSICAL CHARACTERISTICS OF RESERVOIR ROCKS

Secondary oil reservoirs in Jurassic terrigenous deposits of the MO are related mainly to two facies groups: proluvial—alluvial arenaceous coarse fragmental and lagoonal—marine nearshore shallow-water siltstones—sandstones. Such unique lithofacies control is determined by the fact that precisely these two groups for different reasons (low sorting and high degree of compressional compaction, early silicification and carbonate cementation) are represented by the most strong and dense rocks subjected subsequently to the most intense transformations within the DSZs. The combination of the initial lithofacies diversity with the diversity of factors and "mechanisms" of decompression determined the complexity of the structure of the void space of secondary reservoirs, in the formation of which in various combinations participate

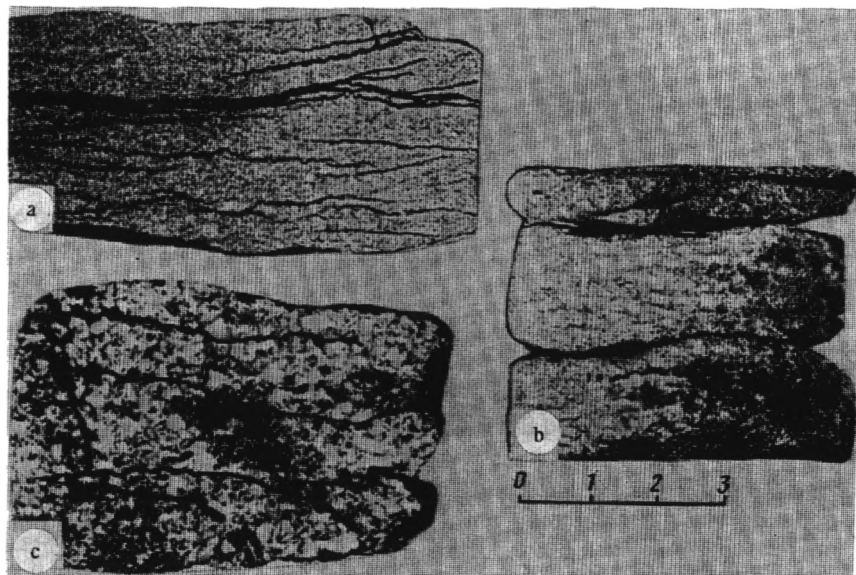


Fig. 2. Characteristic types of fractures in oil-bearing clastic rocks of the producing horizon YuK₁₀ of the Sherkaly suite (Tala area): a) series of stylolitized fractures formed during natural hydraulic fracturing of the reservoir (with opening of bedded jointing) of well 7612, depth 2707-2715 m, 1.35 m from top); b) disklike jointing in core of homogeneous medium-grained sandstone (well 4987, depth 2682-2692 m, 2.5 m from top); c) open jointing in gradient with massive texture (well 7233, depth 2700-2710 m, 0.85 m from top).

various types of fractures, caverns, and secondary pores. The Jurassic oil reservoirs differ from the terrigenous reservoirs of the Cretaceous oil- and gas-bearing complexes only by the wider range of reservoir properties, far more complex morphology of the void space, and pronounced anisotropy of the flow and storage properties due to various genetic types of fracturing (Fig. 2).

Dilatant Microfracturing. Dilatant prefractioning was presumed [1] as one of the main prerequisites for the formation of secondary interstices in Jurassic rocks within the DSZs. These presumptions were based mainly on known experiments (W. Beckhofen, D. Handin, and D. Griegs, N. N. Pavlov et al.) on fracturing of various solids (including rocks, concrete, etc.) and data on seepage of oil from hydrophobic bituminous Bazhenovo rocks with a dense matrix and reversible fracturing. As is known, dilatant fracturing has mainly a reversible character (closing of microfractures with removal or decrease of geodynamic stress), in connection with which it is difficult to establish it in sedimentary rocks. However, on the basis of known experimental and theoretical positions of the strength of materials, its imprint should be expected in the form of residual microfracturing in the most brittle rocks or minerals. The use of the metallographic photomicroscope "Neofot" made it possible to establish the wide distribution of this genetic type of microfracturing. In particular, it is characteristic for fanglomerates that experienced dilatant prefractioning and for other maximally petrophysically inhomogeneous rocks, being localized in fragments of siliceous rocks, large inclusions of quartz, feldspars, etc. (Fig. 3). Of extreme interest here is the presence of such fracturing in fragments that underwent corrosion, regeneration, and other signs of the action of hydrothermal fluids, which indicates a multiphase pulsating character of hydrodynamic stresses and hydrothermal processes in DSZs. It should be emphasized that these local areas of microfracturing in the largest rock components should be regarded only as an indicator of dilatant prefractioning. Dilatant fracturing itself is far more widespread in rocks. Evidently, cataclasis of quartz grains, the degree of which demonstrates a direct dependence on the content of hydrothermal mineralization, is to a considerable extent related to it [11]. As for pelitomorph members and interlayers, it is displayed in them only in the case of changes in the stress state caused by various factors (including technogenic — coring, cutting the core, etc.).

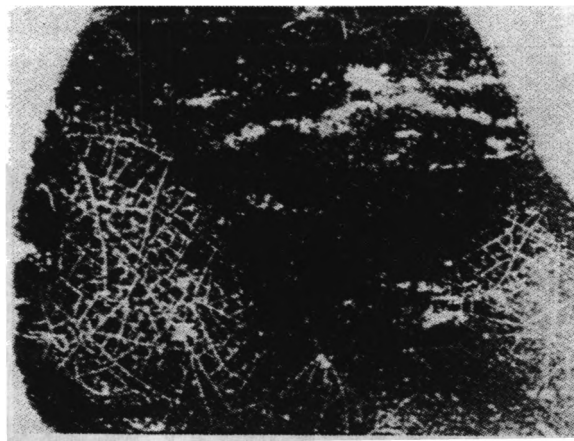


Fig. 3. Character of localization of dilatant fracturing (fragments of nonuniformly microfractured phthanites in oil-bearing secondary porous gravelstone. Tala well 5070, depth 2691.9 m). Taken in reflected light on the "Neofot-2" photomicroscope, magnification 22.

Thus the earlier presumed [1] dilatant prefracturing of rocks within the DSZs should be regarded as a real litho-physical process, the main consequence of which is initial decompression and weakening of the rocks, facilitating subsequent intrusion of deep-seated fluids. At the same time, these observations show how petrophysical inhomogeneity delays the process of growth of dilatant microfractures into main microfractures. This process is initiated by the intrusion of high-energy (high-pressure, high-enthalpy) fluids, which leads to opening of all blind joints and to phenomena of natural hydraulic fracturing (NHF).

Stylolitized Fractures of NHF. Stylolitized fractures are rather widespread in Jurassic rocks, being localized, as is characteristic also for other sedimentary complexes [10], not only in carbonates but also in siltstones and sandstones. However, unlike the deep-seated (deeper than 4 km) Lower Carboniferous horizons of the Dnepr–Donetsk basin or Middle Devonian horizons of the Timan–Pechora province, here are developed mainly feebly expressed fine-tubercular parastylolites as well as insignificantly stylolitized fractures along the bedding surface. A general feature of these sub-horizontal, mainly closed fractures developed not only along newly formed NHF fractures but also along various weakened surfaces (bedding, diastems, lithogenetic fractures) is the presence of a film ("lining") of a dark-colored pelitomorphous polyminerale substance (DPPS). The main components of the DPPS, to judge from the x-ray diffraction, IR spectroscopy, and electron microscopy data, are solid carbonaceous phases of the anthraxolite and shungite type (temperatures of formation greater than 350°C), clay minerals (kaolinite, dickite, hydromica, chlorites, mixed-layer, and smectites), carbonates (ankerite, etc.), sulfides (pyrite, sphalerite, etc.). The considerable mineralogical diversity is combined with poor crystallinity. Undiagnosed mineral phases are noted, the presence of native minerals and intermetallic and organometallic compounds is possible. A polyminerale character in combination with a low degree of crystallinity and presence of metastable phases indicates high rates of crystallization. Such "frozen mixtures," as was shown earlier [10, 11], occur in hydrothermal ore-forming systems with "choking" the deep-seated fluids under conditions of pronounced pressure and temperature drops as a consequence of their extremely rapid rise and intrusion. The specific features of the DPPS are displayed still more markedly in its geochemical study. The data of quantitative spectral and x-ray fluorescence analyses indicate abnormally high concentrations of uranium, thorium, boron, mercury, REE (lanthanum up to 0.002%, cesium up to 0.002%, ytterbium up to 0.005%, yttrium up to 0.002%), chromium (up to 0.045%), titanium (up to 1.8%), zirconium (up to 0.35%), vanadium (up to 0.1%), nickel (up to 0.04%), zinc (up to 0.03%), barium (up to 0.06%), strontium (up to 0.1%) as well as high contents of copper, lead, niobium, tin, etc. The formation of this abnormal "incoherent" geochemical association, including sidero-, chalc-, and lithophile elements, unambiguously indicates a deep-seated character of fluids, to which are related phenomena of NHF and opening of rocks along weakened zones (open older joints, lithogenetic fractures, bedding surfaces, etc.). This is confirmed also by isotope-geochemical features*. Thus, the isotopic

*All isotope data given in this works are based on determinations made by F. I. Berezovskii in the laboratory of stable isotopes, Department of Metallogeny, Institute of Geochemistry and Physics of Minerals, Ukrainian Academy of Sciences, with the use of mineralogical fractions selected by A. E. Lukin.

composition of sulfur of the DPPS corresponds to the meteorite-troilite standard ($\delta^{34}\text{S}$ from -0.4 to $+0.55\%$), which is characteristic for volcanogenic pyrite and hydrothermal ores. The isotopic composition of organic carbon varies from -21.8 to -25.7% , i.e., substantially heavier compared with coal inclusions ($\delta^{13}\text{C}$ -28 to -32.5%), petroleum hydrocarbons (-29 to -32.4%), and especially gaseous hydrocarbons (more than -40%). However, it fits completely in the range of $\delta^{13}\text{C}$ values (-19.5 to -25.8%) of solid bitumens (anthraxolites, thucholites, etc.) of hydrothermal mineralization [2] and on the whole corresponds to the carbon isotopic composition of shungites (-23.1% to -29.8%).

The characteristics of the composition of the DPPS indicate that it most completely reflects the geochemistry of the original fluids. This is consistent with the fact that fractures with DPPS (including fine-tubercular stylolites and simply closed fractures without noticeable traces of stylolitization) belong to the earliest fractures compared with other mineralized (by carbonates, quartz, dickite and kaolinite, sulfides, solid bitumens, etc.) fractures. Thus all forms of segregation of DPPS characterized above are indicators of hydraulic fracturing of the formation to a far greater extent than other types of hydrothermal mineralization (carbonate, quartz, and other crystalline-granular aggregates in the form of veins, streaks, pockets, etc.).

Practice of artificial hydraulic fracturing, which is carried out usually under conditions of a minimum excess of pressure of the fluid injected into the well above the formation pressure, shows that in rocks without subvertical and diagonal fractures and weakened surfaces, fractures occur mainly along sheeting structures, along the bedding surfaces. The width of these fractures reaches one to several centimeters, the permeability and fluid conductivity of the formation increases by one or two orders and more [4]. However, with removal of the pressure of the injected fluid their openness decreases to complete closure. Thus, occurring as a NHF fracture, the given morphogenetic type of fracture at the time of its formation was a briefly existing but extremely effective (with the possibility of repeated renewal) fluid conductor. However, after closing, these fractures owing to the presence of a pelitomorphous lining become practically impermeable in a direction normal to the bedding (but not along the bedding!), which, first, markedly increases seepage anisotropy and, second, substantially affects the distribution of the pore pressure in the reservoir. The least permeable of the fractures of the given type - slickolites, representing microthrust surfaces with traces of displacement (millimeters, centimeters, and sometimes a few meters) in the form of slickensides and striae - especially intensely affect the redistribution of pore pressure in the reservoir. As a consequence of this, the magnitude and size of the pore channels within the pelitomorphous lining markedly decrease, thanks to which it, despite the inconsiderable thickness, has large breakthrough pressures (> 12 MPa, pores in cross section $< 0.01 \mu\text{m}$) and very low ($< 1.02 \cdot 10^{-21} \text{ m}^2$) gas permeability. In a number of cases slickolites completely isolate the oil reservoirs from water-bearing reservoirs or separate reservoirs and nonreservoirs.

Open subhorizontal fractures are most completely developed in the central and southern parts of the Tala area. The dominant directions of dip of the fractures, established from a set of criteria with the use of the core orientator of the Institute of Geology and Geophysics, Belarus Academy of Sciences (V. A. Moskvich et al.), are: 1) $270-295^\circ$; 2) $60-100^\circ$; 3) $300-350^\circ$ (the dip angles vary from 8 to 63°). Fractures mineralized in various degrees (with carbonates, solid bitumens, DPPS, etc.) are found along with fractures completely open and in various degrees oil-bearing (filled with oil; containing coatings of oil and resin-asphalt components; without explicit oil shows but with signs of hydrophobization). The linear density of fracturing varies in very wide limits: from $50-100$ to $500-800$ 1/m. Naturally, its regular relation to primary textural features of the rocks is observed (high values in rhythmities, subhorizontal wavy-bedded siltstones and fine-grained sandstones). However, in a number of cases its markedly increased (to 200 1/m and more) linear density is noted in massive arenaceous formations, which is clearly manifested in the divisibility of a core into disks, the thickness of which varies from $3-5$ to 0.5 cm and less (see Fig. 2). Such intervals are related paragenetically to closed, often variously (usually weakly in the given complex) stylolitized fractures mineralized with DPPS (see Fig. 2) and/or with poorly permeable clay interlayers. This indicates that the nonuniform distribution in the section of pore pressure and its abnormal increase in certain intervals play a large role in the formation of open fractures. There exists another interpretation of this phenomenon in the oil-bearing rocks of the Tala field [5], according to which the divisibility of the core into disks ("pancakes" in the terminology of M. Yu. Zubkov et al.) is due to hydrothermal leaching of the clay partings. Here the generally known facts of the wide development of the given phenomenon in the most diverse rocks masses in a tectono-geodynamic stress state (zones of disklike jointing in Precambrian crystalline rocks of the Kola superdeep zone, in massive carbonate overpressured reservoirs at the Karachaganak and other fields of the Caspian region, in sandstones of the outburst-hazardous zones of the Donetsk coal basin, etc.) are not taken into account. In the given case this also should be regarded as a indicator of tectono-geodynamic stress. And since the degree of the latter is considerably lower than in the examples given above, the intensity of manifestation of disklike jointing in Jurassic rocks of the Tala and other areas is

affected to a far greater extent by primary (presence of rhythmites, etc.) and secondary (presence of intraformation fractures with poorly permeable "linings" of DPPS) textural features. As for hydrothermal leaching of clay partings, carbonate concretionary interlayers, etc., the formation of fractures and caverns is related to this.

The system of fractures formed as a result of the action of the indicated factors is regularly related to the vein-stratiform character of the oil potential of the Jurassic terrigenous deposits and determines the pronounced seepage anisotropy of the producing horizons.

Fracture-Caverns. Along with plane-parallel fractures, the openness of which is 10-15 μm (measurement in lumps by means of the "Neofot" microscope), the presence of fracture-caverns was established. A study of their morphology compared with diverse forms of mineralization (veins, pockets, streaks, etc.) indicate that the formation of the given type of fractures is due to: a) a combination of the NHF mechanism with active leaching of the walls by corrosive hydrothermal fluids and/or b) processes of leaching both of "primary" clay and carbonate inclusions and of fractures and caverns mineralized earlier (by carbonates, clay minerals, etc.). Their characteristic features are pronounced variations of openness (from 10 to 200 μm and more) and transition to opening or closing of fractures of another morphogenetic type. Unlike the described open fractures, the contribution of which to the overall secondary voids of the rocks ("fracture porosity") varies from 0.01 to 0.5% depending on linear density, an increase of the storage properties by 5% and more can be related to fracture-caverns (in the case of their sufficiently intense development).

STRUCTURE AND AUTHIGENIC MINERALS OF THE PORE SPACES OF RESERVOIR ROCKS

The wide distribution of fracture-caverns figuring in the characterized fracture system and at the same time directly related to secondary porosity is a clear confirmation of the leading role of high-pressure (NHF phenomena), high-enthalpy (intense leaching and metasomatism) deep-seated fluids in the formation of oil reservoirs of the given type. The structure of their voids radically differs from the structure of the pore space of the traditional type of terrigenous reservoirs represented by sandstones with a high degree of sorting and roundness of clastic material. Morphologically complex pores of an explicitly corrosion nature are characteristic for them. Their other characteristic features include: a very wide range of flow and storage properties (I-VII class of reservoirs according to the classification of A. A. Khanin—I. A. Mukharinskaya) and the absence of one clearly expressed peak on the pore-distribution curves. The data of a study of the morphology of their pore space (mercury porosimetry, scanning electron microscopy) indicate that the size range of pore channels increases as a result of their enlargement with increase of the intensity of reworking of rocks, which is accompanied by an increase of flow and storage properties. Complication of the structure of the pore space compared with its initial structure, determined by particle size and sorting of the terrigenous material, is observed simultaneously (Fig. 4). Most of the investigated reservoirs of the given type are characterized by a very broad (0.01-100 μm and more) range of pore sizes. Here genetic and age heterogeneity of the pore space is clearly established on the basis of a stage analysis of authigenic minerals. Pores with a size less than 8-10 μm , which corresponds to values of the lower limit of effective porosity and permeability of oil reservoirs, are relics of the primary (formed in sedimentogenesis—diagenesis—early catagenesis) pore space. Diagenetic—early catagenetic glauconitic hydromicas, ferruginous chlorites, and smectites are mineralogical correlatives of subcapillary pores, to which is related residual water saturation. Pores of the interval 10-100 μm and higher, to judge from their morphological features, are related to leaching of clay and carbonate cement, various fragments (quartz, feldspars, micas, etc.), microinjections (glauconite, carbonates), and secretion-vein fillings (carbonates, quartz, clay minerals). The maximally reworked terrigenous (usually inequigranular and coarse-fragmental) rocks are dickite—kaolinite—quartz metasomatites with a complex pore space and wide development of large (> 50 μm) pores and caverns). The magnitude of secondary porosity varies in wide limits (from 3 to 20% and more) depending on the initial sedimentation characteristics of the rocks, regime and intensity of hydrothermal reworking, mineral composition, and quantity, structure, and physicochemical properties of the newly formed mineral aggregates.

Thus minerals of the kaolinite group and quartz are among the most important mineralogical indicators of secondary reservoirs. Here it is necessary to take into account the presence of their various generations related to different stages of lithogenesis.

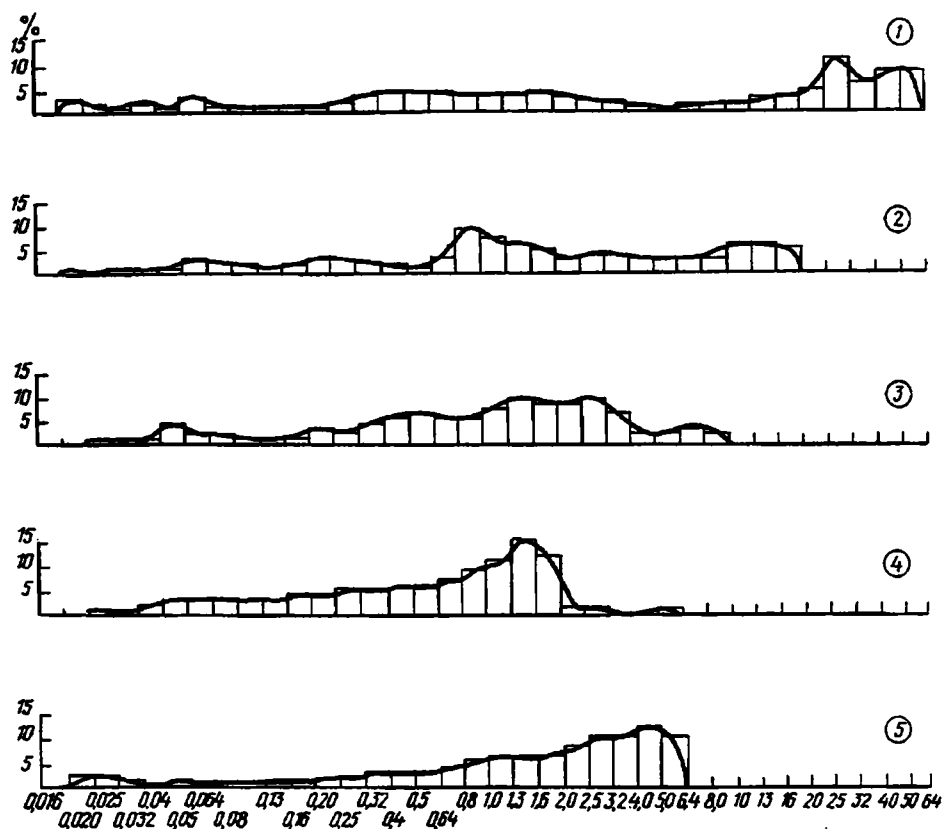


Fig. 4. Characteristics of the structure of the pore space of clastic rocks of the Sherkaly suite of the Tala area according to the mercury porometry data: 1) class I reservoir (cavernous – porous siliceous rock – quartz gravelstone with dickite and druses of hydrothermal quartz crystals in secondary cavities, well 7612, depth 2665 m); 2) class II reservoir (inequigranular porous quartz sandstone with triclinic kaolinite, dickite, and hydrothermal quartz in secondary pores, well 7612, depth 2658 m); 3) class III reservoir (graywacke – quartz fine- and medium-grained sandstone with primary monoclinic and secondary triclinic kaolinite, well 76123, depth 2707 m); 4) (well 7612; depth 2699 m); class V reservoirs (poorly permeable polymictic fine-grained sandstones with allothigenic chlorite – hydromica – kaolinite matrix without signs of hydrothermal alterations, well 4987, depth 2705 m).

Among minerals of the *kaolinite group* are distinguished two main generations markedly different both in crystal-chemical features and in petrophysical role. The I generation, represented by metahalloysite and structurally disordered monoclinic kaolinite, is especially characteristic for continental coal-bearing dense sandstones and siltstones, the pore space in which is often completely plugged by clay material of the "fireclay" type. The II generation, the composition of which includes triclinic perfect kaolinite (value of the order coefficient 0.90-1.35) and dickite, is typical for coarse-fragmental and arenaceous rocks with explicit petrophysical (various manifestations of anisotropy, fractures, secondary cavern porosity and porosity) and with mineralogical and geochemical signs of hypogene metasomatism. In addition to the generally known crystal-chemical and structural-aggregate differences, these generations markedly differ from one another in: a) physico-chemical properties (the heat of wetting and specific effective surface with respect to water and benzene for the substance of the I generation are respectively 4.5-6.8 cal/g and 150-200 m²/g and 36-45 m²/g and for the II generation 1.8-2.1 cal/g and 65-75 and 15-18 m²/g); b) oxygen isotopic composition (for the I generation the value of $\delta^{18}\text{O}$ is equal to 14-16‰ and for II, 9.5-10‰); c) correlation with other rock components (with a pronounced mutual antagonism in distribution). In particular, a distinct direct relation is observed between the concentration of triclinic kaolinite (dickite) in the pore space and content of leucoxene and cataclastic quartz, whereas such relations are not characteristic for the I generation. This has a clear-cut genetic sense, since the process of intense leucoxenization of ilmenite, sphene, and other titanium minerals is one of the mineralogical – geochemical indices of the effect of hydrocarbon-forming fluids on rock [12], and cataclastic quartz (with cloudy extinction, Boehm lamellae, etc.) is one of the most keen indicators of tectono-geodynamic stress.

Structural-generation, physicochemical, and isotope-geochemical unity of triclinic perfect kaolinite and dickite indicates an identical mechanism of their formation by synthesis from thermal fluids enriched in silicon and aluminum. More complex are problems of the paragenetic relations between triclinic structurally ordered kaolinite and dickite and evaluation of the role of the latter as an indicator of oil potential. As shown by the data on the regularities of the oil potential of deep horizons of the Dnepr-Donetsk, Timan-Pechora, and other provinces, precisely the presence of triclinic perfect kaolinite in deeply buried (at depths greater than 4 km) sandstones is the main mineralogical indicator of an oil reservoir, whereas dickite there usually is a sign of strongly altered nonproductive rocks. This rule for the given complex is in need of corrections, since here in certain specimens of oil-bearing sandstones, along with triclinic kaolinite or even in place of it is established dickite, which is also concentrated in the coarse-pelitic fractions, forming various intrapore aggregates in secondary reservoirs (Fig. 5). A study of stage relations between dickite and triclinic kaolinite and data of experimental investigations on transformations of phyllosilicates at high pressures and temperatures [17] indicate that precisely triclinic ordered kaolinite is the most stable mineral of the given group, forming together with oil the latest generation in secondary reservoirs. Dickite, the formation of which with respect to a number of features is related to the highest-temperature hydrothermal fluids (up to 260-280°C) for the given fluid-rock system, during subsequent cooling was to a considerable extent transformed to triclinic kaolinite. In many cases the process of this polymorphic transition did not reach the end. Thus, for Jurassic productive complexes of the MO and mainly for the Sherkaly-Tyumen complex, dickite should be regarded jointly with highly ordered triclinic kaolinite as a mineralogical indicator of secondary oil reservoirs. Here it is expedient to distinguish two aspects. From a petrophysical (physicochemical) viewpoint their presence owing to minimum hydrophily and surface activity compared with other clay minerals as well as due to the loose porous structure of the aggregates (see Fig. 5) worsens the flow and storage properties comparatively less, although their high content indisputably numbers among negative factors. However, from an exploration viewpoint the presence of dickite and triclinic kaolinite both together and separately is unconditionally a positive sign of hydrothermal alteration of terrigenous rocks originally compacted and devoid of primary reservoir properties.

Quartz is the most widespread authigenic mineral in secondary reservoirs. Several generations of authigenic quartz are present in this case, since the geochemical prerequisites of its crystallization (combination of marked increase of the silica concentration in pore waters with a decrease of pH or temperature) occurred repeatedly at different stages of lithogenesis.

The earliest generation of authigenic quartz is noted in alluvial channel sandstones enriched in coaly material. It is localized as contact-porous segregations and regeneration rims nonuniform in thickness. In the given case its formation is related to expulsion from adjacent clay deposits of silica-enriched waters, the solubility of which markedly decreases in the acid (presence of coaly material, increase of $p\text{CO}_2$) environment of clastic deposits of continental origin. Therefore, early silicification is an important factor of a decrease of primary porosity of siltstones and sandstones and their consolidation. During superposed epigenetic processes in DSZs such early-silicified rocks become a favorable substrate for the formation of secondary reservoirs. In the composition of the latter are noted several generations of quartz differing in temperature, repeatedly regenerating clastic grains and forming geodes of well-faceted crystals. The homogenization temperatures of gas-liquid inclusions of quartz crystals vary from 100-120 to 260-280°C, which indicates repeated pulsating intrusion of hydrothermal fluids and a complex paleogeothermal regime. Intense silicification with complete plugging of secondary porous channels is not characteristic for these rocks. Therefore, hydrothermal quartz can be regarded as an undoubtedly positive factor of formation of secondary reservoirs, since it, first, is associated with the formation of secondary voids (leaching of carbonate, clay, and other material) and, second, promotes strengthening of hydrothermally leached cavernous-porous metasomatites.

Carbonatization is not characteristic in the given case for superposed hydrothermal processes. Only a quite limited formation of *ankerite* (ferrodolomite, siderite) in the composition of certain veins and inclusions is related to it. Hydrothermal carbonates in rocks of the Jurassic complexes and basement markedly differ from diagenetic and protocatagenetic carbonates, for which the value of $\delta^{13}\text{C}$ varies from +3.5 to -0.1‰ and $\delta^{18}\text{O}$ from +27 to +30‰, by lower values of $\delta^{13}\text{C}$ (up to -5.0 to -10‰) and especially $\delta^{18}\text{O}$ (up to +17‰ and lower), often approaching ankerites of hydrothermal-ore veins of Freiberg and Nagol'nyi Ridge in the Donbas. Evidently, during the repeated pulsating arrival of hydrothermal fluids and their spreading throughout the permeable rocks and fractures, carbonatization occurred repeatedly as a consequence of degassing, drop of $p\text{CO}_2$, and other factors of an increase of pH. However, the bulk of the minerals forming in this case dissolved during subsequent intrusion of acidic hydrothermal fluids, including the arrival of thermal hydrocarbon fluids.

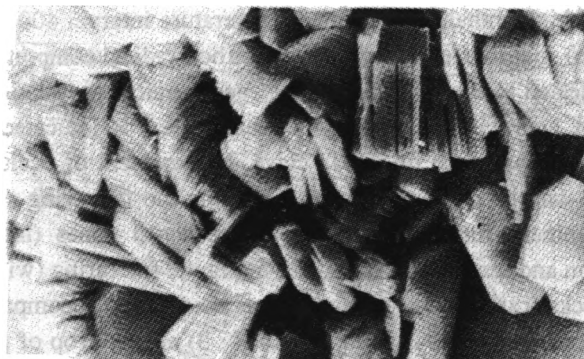


Fig. 5. Dickite in a secondary porous sand reservoir (Tala well 4034, depth 2833-2840 m).

TABLE 1. Informativeness of Authigenic Mineralogical Characters When Separating Clastic Rocks of the Sherkaly Suite Into Two Classes (reservoir – nonreservoir)

Number of character (in order of decreasing informativeness)	Character	Informativeness coefficient
X ₁	Total content of dickite and triclinic kaolinite (fraction > 0.005 mm)	0.932
X ₂	Content of monoclinic kaolinite (fraction <0.001 mm)	0.910
X ₃	Content of secondary quartz (with homogenization temperature of gas–liquid inclusions greater than 100°C)	0.875
X ₄	Total content of hydromica, chlorite, and smectite minerals	0.810
X ₅	Content of carbonate minerals	0.525

The insignificant participation of sulfides in the composition of hydrothermal parageneses indicates a deficit of hydrogen sulfide and thio complexes in the composition of deep-seated fluids. Signs of intense oxidation (with accompanying processes of sulfate reduction in the zone of cryptohypergenesis) of petroleum hydrocarbons are also absent.

Furthermore, regular mineralogical differences between productive and nonproductive (dense or water-bearing) terrigenous rocks create real prerequisites for their use as indicators of oil potential. Secondary oil reservoirs, dense and water-bearing rocks with respect to vectors of the mean values of the content of dickite, triclinic ordered kaolinite, late-epigenetic quartz, leucoxene, monoclinic disordered kaolinite, siderite and calcite, "primary" clay material (hydromica 1M₁, 1Md, mixed-layer – smectites) differ with confidence coefficient 98.5%. Here the informativeness of individual mineralogical indicators (on the one hand, dickite, triclinic kaolinite, and late-epigenetic quartz and on the other "primary" clay material, diagenetic–protocatagenetic carbonates) is so great that even with the use of the linear discriminant method a high (with an informativeness coefficient greater than 0.9) quality of separation of clastic rocks into productive and nonproductive is achieved (Table 1).

PROCESSES OF FORMATION OF SECONDARY OIL RESERVOIRS

All facts presented above indicate that the formation of secondary oil reservoir-metasomatites is a complex multiphase process related to geodynamic activation of DSZs, was accompanied by dilatant prefracturing of rocks and by phenomena of natural hydraulic fracturing and diverse jointing and nonuniformly expressed deep hydrothermal reworking of various types of rocks, and ended with the accumulation of oil.

The first phase of these superposed transformations ended with the formation of a system of NHF fractures (with activation of lithogenetic and sheet jointing) represented by closed, in some cases incipient and weakly stylolitized fractures mineralized with DPPS. The characterized mineralogical and geochemical features of the latter indicate that the phenome-

non of NHF is due to the intrusion of high-enthalpy (presumed temperature interval 400-300°C) carbonate (corrosive with respect to carbonates, feldspars, micas) solutions enriched in hydrocarbon-radical components, organoelemental complexes, silica, alumina, and numerous deep-seated elements ("incoherent" geochemical association). In the composition of gases, along with CO₂ and CH₄ the role of hydrogen was evidently great, which is indicated by the wide distribution of the phenomenon of hydrogen metasomatism (presence of "acid" clays, high content of occluded hydrogen in certain generations of carbonates and quartz). The data given above permit assuming the following sequence of processes of the first phase: 1) intrusion of deep-seated mineral-forming fluids along weakened zones (latent fractures; bedding surfaces, dilatant-decompressed rocks; extension and tension fractures); 2) hydraulic fracturing (with the formation of newly formed fractures) of some of the strongest rocks (carbonates, early-silicified sandstones) accompanied by dissolution of carbonates and kaolinization of feldspars and micas (high pCO₂, low pH values); 3) abrupt drop of pressure (decrease of pCO₂, etc., related to this), dissolution of quartz (owing to an increase of pH with preservation of relatively high temperatures), supersaturation of the fluid, and precipitation of colloidal material; 4) closing of NHF fractures, recrystallization processes, formation of slickensides, etc. Single determinations of the absolute age of DPPS are 25-30 million years (uranium-lead method), which corresponds to the end of the Oligocene - start of the Miocene. Thus, the intrusion of fluids occurred at depths which were 200-300 m less than the present depths with an already formed regional catagenetic zonation. As a rule, insignificant stylolization of fractures mineralized with DPPS as a result of their closing is due to comparatively small (depths < 2.5 km) geostatic pressures. The occurrence of comparatively narrow leaching intervals and system of closed fractures-joints (with pelitomorphic linings) playing the role of intraformation barriers and promoting the redistribution of pore pressures determined the "style" of further fracturing. The latter is determined by activation of DSZs and intrusion of hydrothermal fluids at the neotectonic stage, to which is related the second phase of superposed hypogene transformations. The mainly "stratiform" character of hydrothermal alteration of the rocks indicates a regime of layerwise spreading of fluids arriving along a system of subvertical faults, which is due to the dominance of the geodynamic regime of extension (Fig. 6). Fluids of the second phase, to judge from the complex of new mineral formations and alterations related to them, were represented by low- and medium-temperature (260-120°C) hydrothermal carbonate solutions. Corrosiveness both with respect to carbonates (character of their intense dissolution and leaching), feldspars, hydromicas, and "primary" clay material and with respect to silica minerals (intense dissolution of clastic diagenetic-catagenetic quartz and silicates, formation of secondary quartz) indicate that the high pCO₂ values of thermal waters were combined with a high alkali reserve (owing to the presence of bicarbonates as well as sodium and potassium borates along with sulfates and chlorides). Signs of adularization and albitization also attest to this. At the start of intrusion of hydrothermal fluids mainly their acid character occurred owing to a high pCO₂ and low (to 3-4) pH, which was expressed in intense kaolinization of clastic feldspars, micas, and montmorillonite-hydromica and glauconite clay material. With degassing of the fluids their hydrochemically determined high alkali reserve is displayed ever more strongly, thanks to which their pH could increase to 8-9 with decrease of pCO₂. In combination with the still sufficiently high (> 150°C) temperatures, this promoted intense dissolution, leaching, and redeposition of quartz, as well as sodium and potassium metasomatism. All this provided the maximum realization of the dissolving and leaching functions of the hydrothermal waters with respect to the rocks. Therefore, the formation of secondary reservoirs is related mainly to the second phase, whereas the arrival of oil into these reservoirs occurred later, during cooling of the fluid-rocks system in the Jurassic deposits to present temperatures (i.e., their 100-130°C decrease) and occurrence of a considerable geobaric depression (up to 10-20 MPa), which promoted suction of the hydrocarbon fluids [1, 5]. The problem of determining their sources for the given complex located in the interval between the base of the Bazhenovo suite and top of different-age formations of the Paleozoic intermediate complex and Precambrian crystalline basement is among the most controversial.

A profound geochemical study of crude oils has decisive significance for solving this problem (investigations of V. S. Vyshemirskii, A. É. Kontorovich, S. I. Golyshev, O. S. Stasova, et al.). In particular, the isotope-geochemical indices are informative in this respect. Thus, according to the data of S. I. Golyshev and L. V. Lebedeva (1984), the range of variations of $\delta^{13}\text{C}$ of oils of pre-Cretaceous complexes of central (MO) and southern regions of Western Siberia is: 1) from -30.1 to -34.5‰ (Upper Jurassic deposits); 2) from -27.7 to -31.4‰ (Triassic, Lower and Middle Jurassic deposits); 3) from -28.3 to -30.8‰ (Paleozoic carbonate formations); and 4) from -27.5 to -29.3‰ (regolith of rocks of the crystalline basement and intermediate complex, decompressed igneous rocks). The data of A. E. Lukin and F. I. Berezovskii (1990) indicate a similarity of the oils of the Tala field ($\delta^{13}\text{C}$ from -28.7 to 29.9‰, δD -160‰) to oils from the Var'egan and other fields, the reservoirs of which are confined to Paleozoic and Precambrian rocks ($\delta^{13}\text{C}$ from

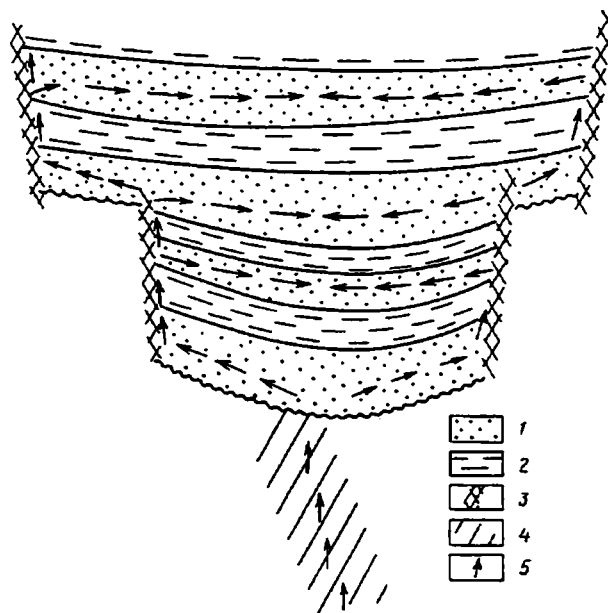


Fig. 6. Basic diagram of movement of hydrothermal solutions in the Sherkaly deposits (according to data of the electrical modeling method): 1) clastic rocks; 2) clays; 3) graben-forming faults; 4) fluid-conducting fault (channel of intrusion of ascending hydrothermal solutions); 5) direction of movement (spreading of hydrothermal fluids).

–28.9 to –30.7‰, δD from –150 to –160‰). Thus the characteristics of the isotopic composition indicate unquestionable similarity of oils of the investigated complex (in particular, the Tala field) to oils from secondary reservoirs in Paleozoic carbonate formations and decompressed crystalline rocks with their explicit difference from oils of the Bazhenovo suite. Consequently, the formation of secondary reservoirs of the Tala type and its filling with oil – these are stages of a single hypogene–hypogenetic process, the terminal phase of which is oil accumulation. However, this does not preclude the possibility in principle of the formation of oil fields of the given type in accordance with another system (descending flow of hydrocarbon fluids and waters as a consequence of their suction into cooling "hydrothermal-vein" reservoirs).

It should be noted that present-day subsurface waters in Jurassic deposits in the Tala, Em-Egovsk, and other areas are characterized by hydrogeochemical diversity, which indicates an unsteady state of the fluid–rock system and processes of mixing of "spent" hydrothermal fluids with subsurface waters. This is confirmed by the data of studying three samples of formation waters taken from Tala wells 5370, 5457, and 5452. Mineralization of these waters is less than 15 g/liter, the hydrochemical type is sodium–calcium bicarbonate–sulfate, which, in general, is usual for the given comparatively shallow complex. On the whole the data of the x-ray diffraction analysis of the phase–mineral composition of dry residues obtained as a result of evaporating these water samples are in accordance with the hydrochemical composition. However, according to the data of x-ray diffraction, differential thermal, and chemical analyses, signs of the presence of celestite, cymrite (barium silicate), alunogen (aluminum sulfate), etc., are noted among salts of the dry residue along with calcium and sodium sulfates and carbonates. The most important is the presence in the composition of the dry residues of a clay-like material represented by dehydrated (evidently as a consequence of overheating of the dry residue during evaporation) halloysite–metahalloysite (reflection 7.69 Å, etc.) as well as amorphous and poorly crystallized phases of the allophane type. This is confirmed also by the high content of silicon and aluminum in dry residues (Table 2). The data on the markedly increased concentrations of boron, strontium, barium, phosphorus, titanium, vanadium, chromium, zirconium, and germanium testify to the specific hydrogeochemical characteristics of these waters, i.e., signs of partial preservation of the anomalous "incoherent" geochemical association, which was so clearly manifested in mineralization products of the first phase of superposed hypogene epigenesis.

TABLE 2. Content of Major and Minor Elements in Dry Residues Obtained as a Result of Evaporation of Samples of Formation Waters Taken in Wells of the Tala Area (according to the data of a quantitative spectral analysis), %

Element	No. of well		
	5370	5452	5457
Calcium	20	20	20
Sodium	5	5	5
Silicon	5	5	7
Aluminum	2	0,5	1,5
Iron	0,1	20	0,1
Barium	0,5	0,2	0,03
Strontium	0,15	0,5	0,5
Magnesium	0,1	0,5	0,2
Manganese	0,0015	0,07	0,015
Titanium	0,05	0,002	0,003
Boron	0,005	0,15	0,007
Zirconium	0,007	0,005	0,005
Nickel	0,0001	0,0005	0,0002
Vanadium	0,0003	0,0003	0,0003
Chromium	0,0001	0,0007	0,0001
Copper	0,0001	0,00015	0,002
Molybdenum	—	0,001	—
Germanium	—	—	0,0002

NEAR-OIL ALTERATIONS AND THEIR ROLE IN PROSPECTING AND EXPLORATION OF OIL FIELDS OF THE GIVEN TYPE

All the data presented indicate that the formation of oil reservoirs in Jurassic terrigenous deposits was accompanied by deep lithophysical, mineralogical, and geochemical transformations of the enclosing rocks with their replacement ultimately by fractured—cavernous—porous dickite—kaolinite—quartz metasomatites. The considerable scale of these processes and deep mineralogical and geochemical transformations caused by them (Fig. 7) at comparatively small depths of occurrence permit counting on the presence here of a system of large direct-prospecting geophysical anomalies. The reflection of these oil-bearing rock masses in the form of "hazy" bands on the common-depth-point time sections established by R. M. Bembel' should be combined, as the results of preliminary calculations show, with negative gravity anomalies. A decrease of the content of hydromica and smectite minerals (to the extent of their complete disappearance in the most oil-saturated secondary reservoirs) was accompanied by a marked change in the physicochemical properties of the rocks and mainly by a marked decrease of their natural electrochemical (diffusion—adsorption and seepage) activity. Along with oil saturation and the aforementioned hydrochemical characteristics, this permits expecting here large geoelectrical anomalies and, consequently, counting on the effectiveness of using electrical methods of prospecting and exploration of oil reservoirs in the given complex.

Substantial changes were noted in the magnetic properties of hydrothermally altered oil-bearing rocks. A pronounced decrease of magnetic susceptibility of dickite—kaolinite—quartz metasomatites compared with the original clastic rocks is due to the combined effect of decomposition of ferri minerals (biotite, amphibole, etc.) and glauconite, leucoxenization of ilmenite, and disappearance of other black minerals widespread here in the form of buried alluvial and beach placers. Consequently, zones of maximum hydrothermal activity and maximum oil saturation should be characterized by distinct geomagnetic anomalies as a result of a decrease of magnetic susceptibility and remanent magnetization of the rocks.

The data of a gamma-spectrometric analysis indicate radical changes in natural radioactivity. The original Jurassic terrigenous deposits are characterized by high values of potassium radioactivity and by the usual range of values of uranium (uranium—radium) and thorium radioactivities for polyfacies paralic deposits. Hydrothermally altered rocks are characterized in various degrees by a marked decrease (to the complete absence) of potassium and increase of thorium radioactivity as a consequence of intense removal of alkalis and accumulation of hydrolyzate elements, which along with aluminum, titanium, etc., include thorium. The contrast of uranium—radium activity increases sharply due to the intense removal of uranium and radium during hydrothermal decomposition of clay material, clastic material, coal inclusions,

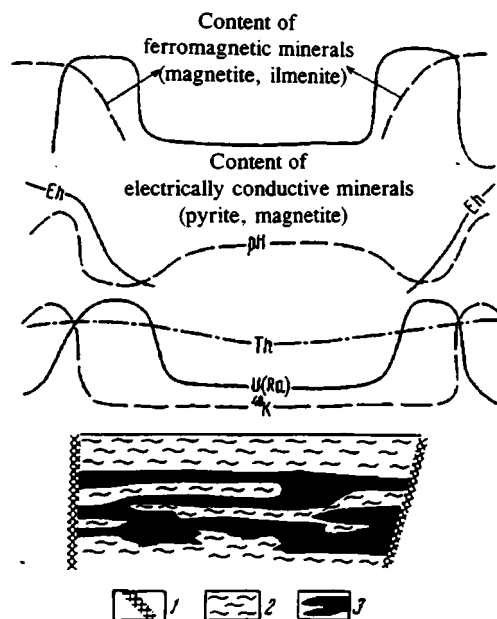


Fig. 7. Basic diagram of alteration of anomaly-forming mineralogical and geochemical parameters in the Tala area: 1) faults; 2) Lower and Middle Jurassic terrigenous deposits; 3) oil reservoirs in hydrothermally altered rocks.

and its accumulation on geochemical barriers of oil–water contacts migrating in time, as well as in solid bitumen mineralization. All this, first, permits counting on a high effectiveness of surface radiometry when outlining zones of maximum hydrothermal alteration and, second, indicates the expediency of conducting spectrometric radioactivity well logging, since other types of well logging do not make it possible to unambiguously single out dickite–kaolinite–quartz metasomatites developed after clastic rocks.

Along with the mineralogo-geochemically determined geophysical anomalies, it is necessary to emphasize the presence here of diverse strictly geochemical anomalies. In particular, the established intense mercury contamination of the oil-bearing and hydrothermally altered rocks [14] and subsurface waters of the productive horizons (works of V. M. Matusevich, A. A. Rozin, et al.). This permits counting on the effectiveness of a gas–mercury survey during oil exploration in Jurassic deposits and basement rocks.

* * *

The data presented indicate a quite complex history of lithogenesis of Jurassic terrigenous deposits of the MO. The degree of their regional (autogenetic) changes corresponds to stages PC_2 – MC_1 . Here the rate of consolidation and ordering of the rocks are largely determined by their primary sedimentation and diagenetic characteristics. The maximum consolidated (strengthened) include: unsorted psephites of the basal layers of the Sherkaly suite, early-silicified coal-bearing and subcoal sandstones (siltstones), sandstones, siltstones, and rhythmities with carbonate cement. Precisely in these rock groups are localized tectono-geodynamic stresses in DSZs and the main manifestations of hydrothermal metasomatism.

On the deposits nonuniformly compacted as a consequence of dia- and catagenetic processes in DSZs are superposed multiphase hypogene processes, including: dilatant prefractioning of the rocks, formation of weakly stylolitized NHF fractures and open quasi-sheet jointing, and hydrothermal alteration of the rocks. This leads to nonuniformly expressed deep petrophysical, mineralogical, and geochemical transformations of rocks with the formation of a system of fractures (the occurrence of pronounced seepage anisotropy) and hydrothermal metasomatites. The dickite–kaolinite–quartz metasomatites developed after polymictic coarse-fragmental and unsorted coarse-fragmental arenaceous rocks of the Sherkaly site have the highest flow and storage properties.

The hydrothermal solutions are distinguished by a combination of a high alkali reserve with markedly increased pCO_2 values (in the absence of hydrogen sulfide and thio complexes), which promoted their pronounced corrosiveness with

respect to both carbonate and silicate—silica mineralogical material. As a consequence of the dominant regime of extension of the grabens, the intrusion of hydrothermal fluids was accompanied by layerwise spreading, with which is associated the primarily stratiform character of the oil-bearing horizons. Vein forms of traps intersecting the original bedding of the deposits are not characteristic for the Jurassic oil-bearing terrigenous deposits of the MO.

The terminal (with respect to all hydrothermal alterations of rocks and new formations) character of oil accumulation does not cause doubts. However, the problem of the hydrocarbon sources is controversial. Variants of their "suction" (as a consequence of tectono-caisson and hydrothermal-adiabatic processes) from the overlying Bazhenovo suite and of arrival of oil-forming fluids from Paleozoic complexes are possible in principle. The available data indicate substantial isotope-geochemical differences of oils of the Bazhenovo suite and Jurassic terrigenous deposits.

Such substantial petrophysical, mineralogical, and chemical alterations of the Jurassic terrigenous deposits and hydrogeochemical transformations of subsurface waters related to multiphase tectono-geodynamic and hydrothermal processes caused the occurrence of a system of associated geophysical and geochemical anomalies. Clear-cut notions about their nature and spatial relationships with oil reservoirs create the prerequisites for increasing the effectiveness of direct methods during prospecting and exploration of fields of the given type both in Western Siberia and in other regions.

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LOWER AND MIDDLE-JURASSIC DELTAIC SEDIMENTARY COMPLEX OF THE NORTHEAST CAUCASUS. PART 2. DYNAMICS ASSOCIATED WITH THE FORMATION OF THE COMPLEX

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In the article, we discuss the deposition of sediments in a deltaic sedimentary complex. We show that the structure of a thick multikilometer terrigenous stratum was as a result of interaction between such factors as downwarping of the basin floor, sea-level fluctuations, and supply of substantial quantities of sedimentary material to the basin by a paleoriver. We estimate actual rates of sedimentation and average rates of deposition of sedimentary sequences. The substantial differences between these rates were caused by numerous episodes of sediment erosion under conditions of vigorous current hydrodynamics.

The Dagestan paleoriver caused the formation of a submarine alluvial fan over an extensive territory of the East Caucasus and, to a substantial degree, determined the structure and composition of a thick sedimentary sequence. It was also responsible for the geochemistry of the deposits. In turn, deposition of the huge mass of terrigenous material brought to the basin had an effect upon the downwarping of the basin floor. Thus, the activity of the paleo-river emerges as an geological factor of cardinal importance in the evolution of the region. In this connection, it is important to assess the temporal and spatial limits of the paleo-delta. As noted in Part I [5], the influence of the paleo-river upon sedimentation was clearly manifest during the Toarcian–Early Aalenian; subsequently, during the Late Aalenian–beginning of the Bajocian, the influence of eustatic transgression and shifting of the delta toward the north or north–east gradually weakened. At the beginning of the Bajocian, tectonic restructuring of the Greater Caucasus region took place, accompanied by rapid transgression of the sea onto the northland, as a result of which the delta shifted to the north by almost 300 km. As a consequence of these movements, the paleo-river had a direct effect upon sedimentation during the Bajocian–Bathonian, primarily within the territory of the North–East Caucasus.

The question of whether or not the paleo-river existed during the pre-Toarcian stage is complicated by the fact that, in the Agvali-Khiva structural-facial zone (SFZ), where deposits show the most clearly expressed evidence of belonging to an avandelta sedimentary complex. Strata older than the Toarcian have not been found. Moreover, in the neighboring SFZ to the south (Fig. 1A), which is separated from the Agvali-Khiva SFZ by a large fault, an Upper Plinsbachian sequence, with a total thickness reaching 3 km, is exposed in addition to Toarcian–Aalenian strata (the base of the Liassic is not exposed). According to data presented in [7], the multiply dislocated Domerian sequence in the most complete section on Keran Ridge includes 8 identifiable cycles separated from one another by sharp boundaries and showing evidence of regression. In the lower parts of the cycles, there are clay shales; higher up, there are interbeds of siltstone and sandstone; finally, at the roof, one finds one or more packets of massive sandstone 10–40 m thick. The cycles themselves are 250–750 m thick. From the east (from Avarsk Koysu, where sandstone content is maximum in several cycles) to the west, the arenosity of the deposits decreases as the thickness of the deposits increases; however, the overall character of the cyclicity persists. From north to south, sandstones and packets containing flyschoid alternations of clay shale and sandstone are succeeded by packets of clayey and banded clayey-silty shales; the thicknesses of the cycles increase in parallel. Thus, the Upper Plinsbachian sequence is generally characterized by the same structural features found for the Toarcian avandelta sequence: cyclicity of a "regressive" type and decreases in arenosity toward the south and west, accompanied by parallel increases in thicknesses of deposits. In this connection, it is quite reasonable to conclude that sedimentation in the northeastern part of the Greater Caucasus basin during the Upper Plinsbachian also proceeded under the influence of a delta, the fore-runner of the Toarcian–Aalenian delta. Moreover, we feel it is quite reasonable to assume the earlier existence of a river system draining the North-East Caucasus region: probably since the time when the Greater Caucasus trough was created, i.e., since the Sinemurian.

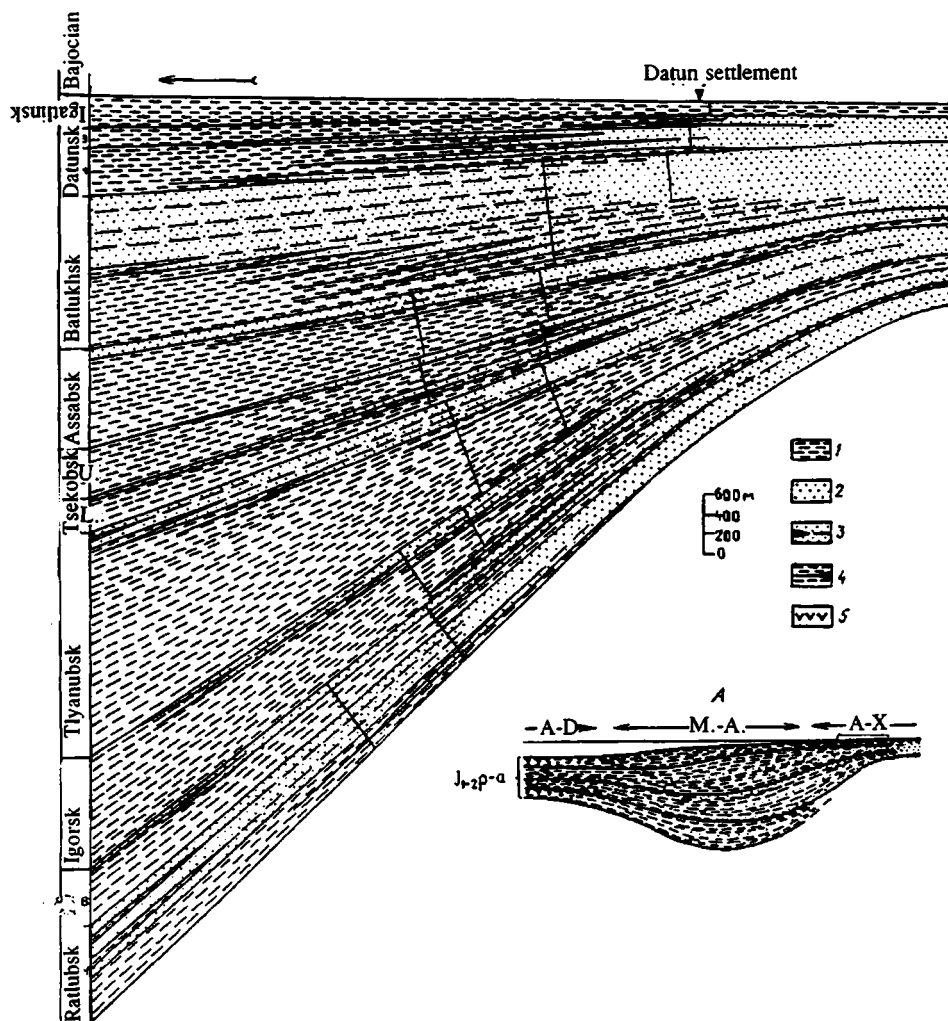


Fig. 1. Diagram showing the structure of the Liassic-Aalenian of Dagestan across the strike of the paleobasin and within various structural-facial zones (A) as well as the structure of the deltaic sedimentary complex within the center of the Agvali-Khiva structural-facial zone (B). 1) Clayey and clayey-silty rocks; 2) sandstone; 3, 4) wedging out and out-of-scale representation of layers (3: layers of clayey-silty rock in sandstone; 4: sandstone and clayey-silty deposits); 5) horizons of tholeiitic basalt lavas and flow-brecciated lavas of tholeiitic basalt in the Alazan'-Dindidagsk SFZ; cuts perpendicular the bedding show approximate positions of the sections of the various suites investigated. For convenience of illustration, increases in suite thicknesses toward the southwest are reduced in the profile relative to the actual gradients of variation in suite thicknesses. The position of Profile B on Profile A is indicated by a bracket. The length of Profile B is ≈ 40 km. Structural-facial zones: A-X) Agvali-Kiva; M-A) Metlyuta-Akhtychaysk; A-D) Alazan'-Dindidagsk.

The territory wherein sedimentary sequences formed under the direct influence of the Dagestan paleoriver was quite substantial in area. Northeast of the region, an avandelta complex extended to the southern margin of the Agvali-Kivsk SFZ, with distal parts of the avandelta penetrating into the Metlyuta-Akhtychaysk SFZ, as evidenced by a number of structural features which suites found in these zones have in common [14]. Thus, within the present-day structure of the East Caucasus, the effect of the Dagestan paleoriver on sedimentation can be traced here and there up to the northern slopes of Glavnny Ridge. In the south, deposits of the avandelta extend at least as far as the Argun river basin. Farther to the west (in the Assa and Armkhi river basins), there is evidence of influx of sandy material from other sources unassociated with the Dagestan avandelta. Evidence for this includes, in particular, changes in the orientation of groovelike sole marks. Accordingly, changes in directions of currents carrying sandy material from southwest and occasionally west in Central Dagestan to predominantly south was probably due to the activity of relatively small rivers flowing from the

TABLE 1. Proportion of Suite Thicknesses in Different Parts of the Deltaic Sedimentary Complex*

Suite	Agvali-Kiva SFZ			Metlyuta-Akhrychaysk SRZ
	Andiysk Koysu-Argun	Avarsk Koysu	Chirakhchay-Samur	
Igatlinsk	100	130	700—950	1000
Datunsk	400—700	420	1400—1900	2500
Batlukhsk	1300	1010—1160	3500	2250—2550
Assabsk	800—850	500	350—700	800—1000
Tsekobsk	700—800	350	?	500—900
Tlyanubsk	1250—1600	1150	?	1000

*Thicknesses are taken from [14] as well as the author's data.

TABLE 2. Variation in Thicknesses of Suites and Subsuites at Various Distances from a Land Paleodelta (the vicinity of the Avarsk Koysu)

Suite, subsuite	Distance between sections, km	Thickness, m		Difference in thickness, m	Thickness gradient, m/km
		northern sections	southern sections		
Assabsk	7	480—500	720	200—220	~31
Tsekobsk	6	340	500	160	~27
Tlyanubsk	4	700	1150	450	~112
*	10	550	1250	700	~70
Upper Plinsbachian	5	190	300	110	~22

*Based upon an estimate by Panov [14].

northland. Interaction between the distal parts of the Dagestan submarine fan and other relatively small, locally occurring fans resulted in relatively complex interrelationships between different geological sedimentary bodies which now cause difficulties in correlating the stratigraphic units of Dagestan with units found in neighboring regions to the west. In fact, the activity of the delta determined the deposition environment over the entire territory of the Agvali-Khiva SFZ. The westward transition from this zone to another, the Digora-Osetiya SFZ was due to a gradual weakening of the influence of the delta upon sedimentation. The region of influence of the Dagestan paleoriver extended from northwest to southeast for no less than 250 km. Of course, there were differences in depositional environment over this extensive territory. As noted in discussions of the structure of an avandelta suite complex [5, 14], thicknesses of suites also vary substantial over the area, increasing from sections relatively near the land delta to more distal sections. This trend is very evident when thicknesses of suites shown in Table 1 are compared. From the vicinity of the Avarsk Koysu River-Karakoysu River to the west and southeast, thicknesses of suites increase 1.5-3 fold. A similar trend can be traced in a southwestern direction; this is clearly evident when comparing sections of deposits belonging to the avandelta complex but accumulated at various distances from the shore (Table 2). On the basis of the regular variation in thicknesses and lithological compositions of deposits [5, 14], the overall structural pattern of the Toarcian-Aalenian sequence over an area of several kilometers in the direction of the more marine parts of the basin (across the strike of the paleoslope) can be presented in the form of the schematic profile (the Avarsk Koysu region) presented in Fig. 1B. Farther to the southwest, there is a further increase in the thickness of the sequence and a decrease in the arenosity of deposits. On the one hand, northeast of present-day exposures of Toarcian-Aalenian deposits, the extend of downwarping decreases and, judging from the average gradient of suite-thickness variation (see Table 2), a region of intensive downwarping over 15-30 km was succeeded, during a different time, by a more stable territory, where a predominantly land-based part of a delta was created in the form of a fairly broad accumulation plain partially subjected to flooding during periods of transgression.

Current models of how sequences (particularly avandelta complexes) are built up suggest that, following the substantial bulging coinciding with the basin-slope zone, there is substantial reduction in thickness with increasing distance

from the shore [12, etc.]. A similar trend holds for J_{1-2} in the East Caucasus: whereas the total thickness of the Upper Plinsbachian (~3000 m [7]) and Toarcian-Aalenian deposits (see Table 1) in the Metlyuta-Akhtychaysk SFZ exceeds 10,000 m, the thickness of deposits of the same age in the Alazan'-Dindidagsk SFZ, correspond to the axial trough of an Early Jurassic-Aalenian geosyncline, is no more than 4000 m [1, 14, 16] (see Fig. 1A). Deposits of the axial trough differ noticeably from those of adjacent SFZs. In Upper Plinsbachian-Lower Toarcian and Aalenian clayey strata here, there are horizons of tholeiitic basalt lava and flow-brecciated lava reaching thicknesses of several hundred meters and accompanied by diabase sills [13]. In addition, in the sequence in the upper reaches of the Lower Toarcian-Upper Toarcian, primarily represented by flyschoid sandy-silty-clayey deposits, there are packets of massive sandstone [13, 16] which are probably related in origin to the activity of the Dagestan avandelta. The increase in thickness of the sedimentary sequence within the Metlyuta-Akhtychaysk SFZ (see Fig. 1) suggests that isostatic downwarping under the weight of avandelta sediments may have taken place here.

The entire multikilometer sequence of Upper Plinsbachian, Toarcian, and Aalenian within the Metlyuta-Akhtychaysk and, especially, the southwestern part of the Agvali-Khiva SFZ is characterized by a special cyclicity resulting from a combination of mostly regressive cycles, with arenosity of deposits progressively increasing upward along the section [5, 7, 14]. Formation of the lower and upper parts of these sedimentary cycles took place in substantially different environments. During its initial stage, a deposit formed against a background of rapidly developing transgression. Next, transgression ceased and was succeeded by advancement of the delta of the Dagestan paleoriver into the water basin. The occurrence of transgression or regression, as well as the rates of such processes and their scales, were determined by several factors.

FACTORS GOVERNING THE DYNAMICS OF FORMATION OF THE DELTAIC SEDIMENTARY COMPLEX

A very thick sequence of terrigenous sediments was deposited over a relatively brief time period (Late Plinsbachian-Aalenian). Formation of the sequence was possible only under conditions of rapid downwarping of the basin floor. Mainly on the basis of the make-up of the Toarcian-Aalenian sequence, we can infer that downwarping took place episodically rather than steadily. Initially, rates of downwarping were maximal. Subsequently, the process slowed or even stopped altogether (Fig. 2, 1). Rapid pulse-wise downwarping of the basin floor was the main cause of the regional transgressions controlling the character of sedimentation during the initial stages in the formation of the first-order sedimentary cycles [5]. Transgressions affected the activity of the delta in such a way as to cause flooding or even general retreat of the delta, accompanied by a sharp reduction in influx of coarse-grained material to the basin; because of this, transgressive episodes were primarily characterized by deposition of clayey-silty sediments. Such factors as supply of substantial quantities of sedimentary material by the river, which tended to build the delta, thus causing growth and advancement of the delta into the basin, had an opposite effect upon shoreline migration and, accordingly upon the development of transgression. In cases of rapid downwarping of the basin, transgression was the dominant process and advancement of the delta began as downwarping slowed or ceased. Such advancement of the delta was accompanied by increased influx of sandy material into the basin. The sandy material substantially enriched the upper parts of cycles formed over a single episode of downwarping.

The interaction of these factors, irregular, pulsewise downwarping and supply of substantial quantities of sandy material by the river, was the main cause of the formation of large first-order rhythms with regressive structure.

Despite substantial similarity in structure, there are certain differences between cycles. For example, different episodes of delta advancement into the basin differed substantially with respect to extend of progradation. In some cases, progradation was relatively slight; in others, it resulted in the formation of thick sandstone sequences which are locally carbonaceous. In addition, some suites (the Datunsk for example) are not clearly regressive in character. These and several other features associated with the formation of different suites were due to the action of yet another factor regulating the dynamics of transgression and regression: eustatic fluctuations of sea level (see Fig. 2, II).

The influence of eustatic fluctuations in sea level in Caucasus basins was discussed previously [4]. It was shown that the largest-scale advancement of the Dagestan delta at the very end of the Toarcian-beginning of the Aalenian was associated with a drop in sea level at that time. This regressive episode can be identified not only in many sections of the

Ammonite zone	Suites	Thickness, m	
		South	North
Sowerbyi	Kunukhsk		
Concavum	Igatlinsk		150
Murchisonae	Datunsk		110 330
Opalinum	Batlukhsk		1100
Levesquei	Assabsk	720	500
Thouarsense	Tsekobsk	260 220	200 160
Variabilis	Tlyanbsk	1200	700
Bifrons	Igorsk	500	
Falcifer	Ratlubsk	180 >400	
Tenuicostatum			

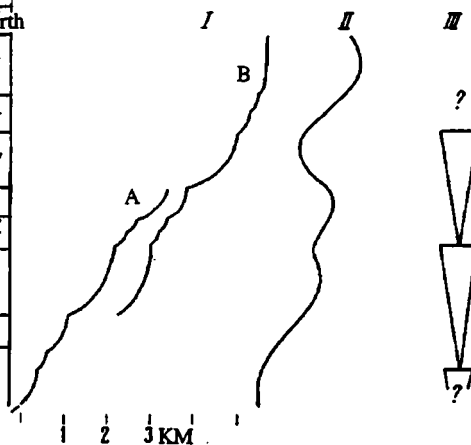


Fig. 2. Diagram showing variations of factors affecting the formation of the sedimentary sequence: I) curves showing downwarping of the Liassic-Aalenian basin floor, plotted on the basis of southern (A) and northern (B) series of sections in the Avarsk Koyusu river basin; II) plot of sea-level fluctuations for the Great Caucasus basin (fluctuation intervals measure several tens of meters); III) proposed supercycles within the structure of the Liassic sequence. In the "Thickness" column on the diagram, the value for the upper part of the suite are given in the numerator and the value for the lower part is given in the denominator.

J₁₋₂ of the Caucasus, but in Western Europe and many other regions of the world as well [4, 24, 25]. Within the North-East Caucasus, substantial quantities of sandy material accumulated during the preceding period at the periphery of the basin began to actively erode when the erosion base lowered and were carried into the water basin, promoting the growth and rapid advancement of deltaic facies into a region of predominantly marine sedimentation. Another episode linked to advancement of the delta into the water basin promoted formation of the essentially sandstone, lower part of the Ratlubsk suite and caused a fall in sea level at the beginning of the Early Toarcian [4, 24]. In the Toarcian section of the avandelta, substantial enrichment with sandy material is also characteristic of the upper part of the Tlyanubsk suite, which, as noted earlier [5], was also deposited in an environment of substantial delta advancement into the basin. This episode can be dated by means of lower reaches of the *Gr. thouarsense* zone and apparently was relatively short-term. A lowering of sea-level actually took place at the same time; this has been confirmed by lithological data from other areas of the North Caucasus. Thus, in several sections of the Toarcian (the Uruk and Ardon rivers) in the Digora-Osetiya SFZ, there is evidence of substantial shoaling of the water basin, in particular, preceding the formation of horizons with bioherms. Based upon ammonite fauna, the period of shoaling can be dated as corresponding to the *Gr. thouarsense* zone (identification by V. P. Kazakova), i.e., has coinciding in time with the deposition of the upper part of the Tlyanubsk suite. Thus, eustatic drops in sea level, in cases when they coincide in time with downwarping of the basin floor, allowed the most substantial advancements of the delta into the basin.

Eustatic elevations of sea level had different effects upon the formation of a sequence; depending upon whether the elevation coincided with a period of rapid downwarping or a slowing of downwarping. For example, the Lower Toarcian Igorsk suite generally formed against a background of elevated sea level. During the initial stage in the formation of the suite, when the basin floor rapidly subsided, both these processes promoted transgression and migration of the delta to the north-east. Subsequently, when downwarping slowed, gradual advancement of the delta into the basin began. This, however, to some degree moderated the on-going eustatic elevation of sea-level. Thus, deposition of strata during this time was affected by processes "of a different sign," exerting influence in the opposite direction. As a result, relatively moderate enrichment of the upper part of the suite with sandy material took place. On the one hand, during the next stage (during the formation of the Tlyanubsk suite), the initial rapid downwarping of the basin floor coincided with continuing and probably accelerating rise of sea-level; this caused a powerful transgression and substantial shift of the delta toward the north-east; as a result, the thickest clayey stratum in the entire Toarcian section was formed (see Fig. 1).

An aggradation plain formed within the more stable territory located to the northeast of the region of rapid downwarping of the basin. This territory was also involved in subsidence during pulses of rapid downwarping in southern parts of the basin, but the subsidence in this case was relatively minor (probably no more than a few tens of meters). Nevertheless, it was sufficient for the development of rapid transgressions. Sea-level fluctuations were comparable in amplitude to the downwarping of the territory; accordingly, their interaction in the same direction or opposite direction substantially affected shoreline movement.

A general reconstruction of the depositional environment of the Liassic-Aalenian sequence of the Northeastern Caucasus taking into account the actions of such powerful factors as downwarping of the basin floor, fluvial supply of substantial quantities of sandy material, and eustatic fluctuations of sea level allow us to propose the following scheme for the formation of the deposits [5].

During the Late Plinsbachian, sedimentation primarily took place against a background of gradual elevation of sea-level and, subsequently, a relatively high stand of sea-level [4, 24]. At present, there is no reliable evidence of abrupt falls in sea level. Since one primarily finds distal facies of the Dagestan submarine alluvial fan in the Metlyuta-Akhtachaysk SFZ, where Upper Plinsbachian deposits occur, not all features associated with the existence of a sedimentary basin find expression in the section of the sequence. Never the less, the regressive-appearing cycles found here [5, 14] allow us to suppose that deposition during this stage in the formation of the avandelta complex was controlled by no less than eight transgressive—regressive cycles.

At the very beginning of the Toarcian, a fairly substantial drop in sea level took place [4, 24, 25]. In association with this episode, delta deposits advanced into the basin; this advancement is clearly identifiable in the section of the Agvali-Khiva SRZ. The Lower Ratlubsk sequence, with a high content of sandy material, formed as a result of this advancement. Subsequently (in the second half of the *D. falcifer* zone, however, a transgression common to the Caucasus as a whole began to develop [4, 8] because of eustatic elevation of sea level, with the upper cycle of the Ratlubsk suite forming as a result. The beginning of the eustatic transgression coincided with a transgression caused by a pulse of basin downwarping, but when downwarping of the basin ceased and the stage of delta advancement into the basin began, the eustatics made the transgression substantially weaker what the transgression during the formation of the lower cycle of the Ratlubsk suite, as a result of which only the foremost parts of the deltaic area with sand deposition reached the former position within the avandelta region. Eustatic elevation of sea-level and the transgression associated with it continued over the extent of the *H. bifrons* zone. During the formation of the Igorsk suite, as during Late Ratlubskian time, this weakened the process of delta advancement. The onset of formation of the Tlyanubsk suite coincided with an ongoing transgression, but the second stage, as mentioned above, coincided with an episode of falling sea level, as a result of which, the early Tlyanubskian transgression and the late Tlyanubsk advancement of the delta proved to be relatively powerful processes causing the formation of a contrastingly constructed cycle.

The eustatic drop in sea level (the *Gr. thouarsense* zone) was followed by a rise, which accompanied the formation of the Tsekobsk suite. The latter consists of two relatively small cycles 150-200-m thick; i.e., both pulses of basin downwarping were relatively small in comparison with the preceding pulse. The cycles are characterized by regressive structure, but with weakly expressed contrast between lower and upper parts. The greater clay content in the deposits of the upper cycle in comparison with the lower was a result of formation of the cycles against a background of eustatic transgression. The last part of this stage of eustatic elevation of sea level, stabilization, and, subsequently, onset of sea-level lowering (in the second half of the *D. levesquei* zone) created the background for deposition of sediments of the Assabsk suite: accordingly, the powerful initial transgression and the delta advancement which followed it were very distinct, in the final analysis; this is because of substantial compositional differences between the lower and upper parts of the suite; i.e., because of contrasting structure.

The substantial drop in sea level at the very end of the Toarcian-beginning of the Aalenian (approximately the second half of the *D. levesquei*-*L. opalinum* zone) resulted in a situation where, despite a powerful pulse of basin downwarping, transgression did not substantially develop and a minor retreat of the delta during early Batlukhsk time was followed by rapid advancement of the delta into the basin. In the vicinity of the stratotype section of the Batlukhsk suite along the Avarsk Koysu River, the suite has the appearance of a distinct, single regressive cycle characterized by appreciable arenosity. We do not rule out the possibility that the predominantly sandy composition of the suite masks the presence of yet another transgressive pulse which could be associated with a sequence consisting of two regressive-appearing cycles comparable to the Batlukhsk suite occurring at the headwaters of the Kazikumukhsk Koysu River.

The elevation of sea level following a fall caused almost all of the Upper Aalenian sequence to be deposited against a background of a developing eustatic transgression. As a result, despite the persistence of pulse-wise downwarping of the basin, advancement of the delta did not occur at the end of the early Datunskian and late Datunskian transgressive episodes, except for at the very end of the Aalenian, when sea-level stabilized for some time (the second half of the Igtalinskian) and the delta advanced somewhat into the basin [5].

Such a pattern suggests how, by the interaction of several factors (downwarping of the basin, eustatic fluctuations of sea level, fluvial supply of substantial quantities of sandy material), large regressive-appearing cycles were formed and why there are differences between the cycles. Whereas the duration of the ammonite zone was approximately 1 million years, the time needed for the formation of these cycles can be estimated as between several hundred thousand years and ~1.5 million years, depending upon the sizes of the cycles. The duration of eustatic fluctuations in sea level actively affected the formation of the cyclic structures can be estimated as a few million years; these fluctuations can be considered third-order eustatic fluctuations [3, 30, 32].

The relationship of terrigenous sedimentation, deltaic sedimentation in particular, to transgressions and regressions as well as the causes of such changes have been discussed and modelled by many investigators [2, 11, 18, 19, 20, 31, etc.]; the investigation of certain objects has led to the discovery of quantitative relationships between downwarping of the basin, influx of sandy material, and eustatic fluctuations [26]. In this stage in the our investigation of the Dagestan paleo-delta, we have been able to determine primarily qualitative relationships between the parameters governing the deposition of the sedimentary sequence. In the future, it is quite possible that we shall be able to provide quantitative estimates.

Large-scale cycles classifiable as subsuites or suites exhibit thicknesses ranging from several hundred meters to a kilometer or more. The following trend is noticeable: the thicknesses of cycles in the Liassic-Aalenian sequence vary predictably along the section (see Fig. 2). In the sequence Upper Ratlubsk subsuite → Igorsk suite → Tlyanubsk suite, the thickness of each subsequent member is greater than the one before. The next sequence, Lower Tsekobsk subsuite → Upper Tsekobsk → subsuite → Assabsk suite → Batlukhsk suite, shows the same pattern. The sequences mentioned, as we have presented them, can be considered as two supercycles (see Fig. 2). Let us turn our attention to the fact that their onsets and ends approximately coincide with eustatic rises and falls of sea-level. The Lower Ratlubsk subsuite, formed during a period of falling sea-level, is probably the crowning element in the preceding supercycle, the lower part of which is not exposed within the Agvali-Khiva SFZ. As for the Upper Aalenian suites, they, like the suites in the lower parts of the supercycles, formed against the background of a developing eustatic transgression, but the tectonic reorganization of the entire Great Caucasus which took place at the very onset of the Bajocian substantially altered the character of downwarping of the basin and a subsequent, otherwise possible supercycle did not form. Moreover, it is interesting to note that, during the Bajocian-Bathonian stage in the development of the North-East Caucasus, the thicknesses of the Lower- and Upper-Kumukhsk, Lower-, Middle-, and Upper-Tsudakharsk subsuites, which can be identified in the J₂bj-bt sequence, occur in the following order: 120 → 130 → 190 → 250 → 650 m (at the Karakoysu River), i.e., a pattern emerges similar to that of the Liassic-Aalenian, when each subsuite was, to one degree or another, thicker than the one before it.

In addition to large-scale, regressive-appearing cycles (first-order cycles) classifiable as subsuites or suites, the Liassic-Aalenian sequence is also characterized by thinner (several tens of meters thick) second-order cycles which also show regressive-type structure [5]. The presence of such cycles in the sections was a result of relatively short-term progradation of zones of sand sedimentation into the water basin. In some cases, such cycles are probably sand lobes of deltas which were able to migrate laterally as a result of changes in the positions of arms of the land delta feeding them; in other cases, such cycles resulted from frontal advancement of the area of sand sedimentation. Such advancement was most typical of the concluding stage in the formation of a first-order cycle. Thus, pulsational increases and decreases in the influx of sandy material to the basin took place against a background of overall delta progradation. For example, the upper (most arenaceous) part of the section of the Tlyanubsk suite can be subdivided into several cycles of 50-70-m thickness (see Fig. 1B) [5] which can be traced over a fairly extensive area (many tens of kilometers). The formation of these cycles may have been a result of the same causes responsible for the formation of the large-scale first-order cycles, i.e., downwarping, eustatic fluctuations in sea level, and variations in the quantity of sandy material supplied by the river. However, fluctuations of this type caused by the factors mentioned were of a substantially different duration, lasting tens of thousands of years. Fluctuations in sea level in such cases should be linked to fourth- or even fifth-order eustatic fluctuations [30]. Downwarping (if it was an important factor), must have been discrete rather than uniform in character. Finally, climatic fluctuations caused by Milankovich cycles, etc. [17, 23, 27, etc.] may have exerted an influence on increases or decreases

in the influx of sandy material to the basin. At present, however, it is difficult to definitely identify which of these factors (or which combination) played a leading role in the formation of second-order cyclicity in the Liassic-Aalenian sequence.

RATES OF DEPOSITION AND THE FORMATION OF SEDIMENTARY SEQUENCES

The nonuniformity and pulsational nature of downwarping and the substantial alterations of the depositional environment during the initial and final stages in the formation of cycles allows us to assume that deposition rates of sediments varied substantially. Whereas analysis of the formation of the large-scale sedimentary cycles suggests the existence of substantial differences between short-term sedimentation rates and rates of deposition of thick sedimentary sequences. We will discuss this problem using the Tlyanubsk suite as an example; this suite is one of the most distinctly expressed first-order cycles.

As noted previously [5], the principal deposits of the lower part of the suite are thin, rhythmic interstratifications of silty and clayey layers in which silty layers show more or less sharply defined soles; upward, they are usually replaced by clayey layers. Silty and clayey layers form a single, very fine rhythm which is overlain by a subsequent rhythm along a sharp boundary. The most probable cause of the formation of rhythms of this type are seasonal (annual) variations in fluvial supply of suspensions of various granulometric compositions to the water basin. Evidence for this also includes the fact that rhythmicity of this type is either absent or encountered episodically in the sedimentation within the area of vigorous effects of the Dagestan paleo-river. The thicknesses of silt-clay rhythms vary from 1 to 6 cm, but rhythms with thicknesses of 3-5 cm predominate. Taking into account post-sedimentational compaction of sediments, the average rate of deposition of these types of sediments can be estimated as 5 cm/yr or ~ 50 m/1000 years. These numbers are quite plausible, as evidenced by the results of analogous investigations of present-day objects. Thus, according to the data of Walker et al. [33], sedimentation rates in delta zones of certain rivers can reach 10-400 m/1000 years. Rates of 2-12 m/1000 years have been obtained for the Mississippi fan [29]. Very high deposition rates of oozy sediments have been found on the shelves of the equatorial region [9, 10], in particular, in pre-delta zones of the East-China Sea [21], and other environments [22, 28, etc.].

Advancement of the delta into the basin during the stage of the suite's formation resulted in a rapid increase in the sedimentation rate. Despite the fact that we have no sufficiently definitive criteria for estimating rates of sand deposition during the Jurassic; we can say, in analogy with present-day environments of avandelta sedimentation, that they were at least several times higher than during deposition of the clayey-silty sediments in the lower part of the suite. However, even for sedimentation rates of ~ 50 m/1000 years and persistence of stable, uniform sedimentation rates, several hundred years would be required to fill this entire space within of the basin, space formed during downwarping of the floor (the thickness of the Tlyanubsk suite in the stratotypic section equals ~ 1200 m). In actuality, the Tlyanubsk suite was deposited over a period of no less than 1.5 million years (based upon the 1-million-year duration of a single ammonite zone). Taking into account the thickness of the suite and the time of its formation, we can estimate the rate of sediment deposition as ≈ 80 cm/1000 years; when compaction is taken into account, we obtain rates of 120-160 cm/1000 years. Thus, the short-term rate of the suite's deposition which, actually exceeded 50 cm/1000 years, was more than an order of magnitude higher than the mean total rate of deposition of the suite. Even when acknowledging the approximate nature of the calculations, we can see that the deposition rates substantially exceeded the deposition rate of the sedimentary sequence as a whole [6].

The reasons for this discrepancy are quite understandable if we keep in mind the large numbers of erosional surfaces and scour marks of previously deposited sediments which are found over almost the entire section of the Liassic and Aalenian sequence. Thus, in the lower clayey-silty part of the Tlyanubsk suite, we can trace many levels coinciding with troughlike sand bodies with eroded soles cutting into underlying deposits. The formation of such a level began with an increase in current hydrodynamics in a specific part of the alluvial fan; this was accompanied by scouring of previously deposited sediments to depths ranging from a few decimeters to a few meters as well as development of trenches and current grooves of down-slope orientation. Next, there was typically vigorous infilling of troughs with sandy-silty material. Accordingly, deposition of background clayey-silty sediments was suspended for some time in these parts of the submarine alluvial fan. Subsequently, sedimentation was renewed and could take place more or less uniformly until the emergence of the next erosional level. Taking into account that erosional levels are spaced at distances of several decimeters to several meters (occasionally a few tens of meters), we can speak of interruptions in the deposition of the sequence. Thus, by comparing rates of sediment deposition within different-sized intervals (for example, within several decimeters and within

several tens of meters), we can see that the size of an interval approximates the actual rate of sediment deposition in the first case but reflects an overall pattern of a discontinuous deposition of a sequence, including episodes of erosion and cessation of background sedimentation, in the second case.

During this stage in the formation of the suite, when advancement of the delta into the basin was occurring and was accompanied by influxes of large quantities of sandy material, the difference between the deposition rates of sandy sediments and that of the sedimentary sequence as a whole increased. Actually, the deposition rate of sandy sediments in such an environment may reach decimeters or even meters per year; this substantially exceeds the rate of formation of clayey-silty sediments. Similar rates of deposition have been found in certain areas of present-day avandelta sedimentation. In addition, the intensification of current hydrodynamics associated with subaqueous fluvial flow resulted in frequent and deep scouring of accumulated sediments: in sandstone horizons, there are numerous layers with fragments of different locally found rocks almost all of the sandbeds overlie such layers along sharp erosional boundaries. These structural features of the sandstone horizons suggest high annual rates of sediment deposition and substantially lower rates of deposition of the sequence as a whole. In general, we find the following trend: as deposits of first-order cycles accumulated, sedimentation rate increased and the rate of deposition of the sequence as a whole decreased.

We believe that a similar pattern of deposit formation was typical of all the regressive-appearing cycles identifiable in the Toarcian-Aalenian sequence.

Estimation of the basin bathymetry during deposition of various types of sediments indicates that there are deposits formed at appreciable depths in the J₁₋₂ section of the alluvial fan (within the Agvali-Khiva SFZ). Numerous structural-textural characteristics of deposits suggest that the uppermost sandstone parts of large-scale regressive cycles formed at shallow depths, ranging from several tens to a few meters at different times [5, 15]. During deposition of the lower parts of cycles, the basin depth increased as a result of rapid downwarping of the basin. However, it could not have exceeded the thickness of the cycle, since relatively shallow-water conditions again prevailed at the end of the cycle's formation. The thickness of the cycles indicate that the maximum depth of the basin during deposition of the clayey strata probably reached several hundreds of meters during some stages, but rapidly decreased because of high rates of sedimentation.

Since compensatory filling of the basin with sediments took place at the end of the formation of first-order cycles (this is true of the study area); the computed overall deposition rate for various cycles can be considered an averaged value for the rate of downwarping of the basin. For example, as already mentioned for the area of the stratotype section of the Tlyanubsk suite, the overall deposition rate equals ≈ 1 m/1000 years; however, taking into account that downwarping was most rapid during the initial stages in the formation of the rhythms, the rate of downwarping probably reached several meters, possibly even several tens of meters per thousand years at that time.

* * *

Thus, in summing up the above-proposed scheme for the development of the deltaic complex, let us note the following.

Over the duration of the Late Plinsbachian-Aalenian, sedimentation in the northeastern part of the Caucasus basin (it is quite possible that the Great Caucasus trough evolved from the very beginning of the Jurassic) was governed by a large river forming a deltaic complex of substantial size. The delta's activity was, in many respects, controlled by the such factors as downwarping of the basin floor, fluvial supply of large quantities of sandy material, and fluctuations of sea level. The downwarping was pulsational. At the beginning of each pulse, the rate of downwarping of the basin was maximal, but subsequently downwarping slowed and possibly even ceased. Accordingly, a rapid transgression causing a shift of the delta toward to northeast took place at the beginning stage of each pulse. This stage was characterized by deposition of predominantly clayey-silty sediments in the vicinity of the avandelta. Subsequently, with slowing of downwarping and as a consequence of fluvial supply of substantial quantities of sedimentary materia), growth and advancement of the delta into the water basin took place. As a result of the downwarping of the basin in combination with the activity of the paleo-river, large-scale (many hundreds of meters — kilometers or more) sedimentary cycles with regressive-type structure were created within the avandelta. The intensity of downwarping increased toward the southwest. Lowering or elevation of sea-level (mainly eustatic), depending upon their relationship with different stages of basin downwarping, may have variously influenced the character of sedimentation: a) increasing transgression when a stage of intensive downwarping of the basin of the basin floor coincided with a eustatic elevation of sea-level; b) promoting very substantial advancement of deltaic deposits into the basin during eustatic drops in sea level and slowing or stopping of basin-floor

downwarping during that time; c) blurring of contrasts between depositional environments at the beginning and end of a pulse of downwarping of the basin when downwarping and sea-level fluctuations are antagonistic in their effects upon the development of a transgression or upon advancement of the delta. Actual sedimentation rates and average rates of deposition of whole sedimentary sequences substantially differ because of numerous episodes of scouring of previously deposited sediments.

Indigenous, local tectonic movements as well as differences in the overall (absolute) extent of downwarping of the basin floor over the extensive area occupied by the land delta and avandelta probably affected the redistribution of deposits of sedimentary material and the structure of a sequence. Thus, the development of the delta and avandelta was a function of several factors differing in their degree of influence upon the conditions of formation of a sedimentary sequence, but each of these factors contributed to the process.

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THE EARLY RIPHEAN VOLGA – URALS SEDIMENTATION BASIN

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In the article, we discuss the structure of sections and lateral variation of Lower Riphean deposits of the Volga–Urals regions (from the Samara River to Zlatoust), including the Prikamsk, Borovsk, Bol'sheinzersk, Suransk, and Yushinsk suites. We have systematized all existing literature concerning depositional environments of deposits in the eastern areas of the Russian platform and the western slope of the Southern Urals. On the basis of an analysis of vertical variations of sections and sedimentary textures, we have classified and briefly described sedimentary complexes of various compositions and origin, have pointed out their lateral and temporal relations, and have compiled schematic lithological-paleogeographical maps for the beginning and end of the Ayskian-Prikamskian, Stakinskian-Kaltasin-skian, and Bakal'skian-Nadezhdinskian time intervals. We have reconstructed the main features of the basin and suggest that the basin was near a large, more or less isometric intraplate depression.

Currently, there is increasing interest in synthesizing data from sedimentary basins [35, 56, 58, 61, 64]; this may lead us closer to a solution for the great strategic problem before lithology: construction of a general theory of the evolution of sedimentation basins over Earth's history [52, etc.]. Of course, our sedimentological information is most complete for the Mesozoic–Cenozoic and, in part, Paleozoic basins. In recent years, however, wealth of analogous data has been collected for the Precambrian, especially the Late Precambrian. Here, we may take especial note of the work on the Riphean and Vendian in the Siberian platform [14, 43, 50] and the southwestern Russian plate [8, 25], investigations concerning the Belt supergroup in the western USA and Canada [57, 63, 65, 66], large-scale reconstructions for the Windermere supergroup topping the section of the Late Precambrian in North America [59, 60, 62], and a number of other publications.

The stratotype section of the Riphean on the western slope of the Southern Urals has a somewhat out of place in this series, although it has one significant advantage over the others.* Over the last 10–12 years, it has been fairly completely described in terms of its sedimentology [32, 34], but its status and role in a the largest sedimentation basin, like the Volga–Urals region during the Riphean, has escaped the attention of investigators.† The goal of this report was to synthesize data from sedimentological investigations of intact sections of the Lower Riphean in the Southern Urals and sections in drillholes in the east of the Russian plate (Fig. 1); this was undertaken within the framework of a complex thesis concerning sedimentogenesis and lithogenesis of Riphean complexes of the Urals and analysis of a number of large-scale lithological-paleogeographical maps providing an overall view of the entire evolution of an Early Riphean basin, first of a series of non-coeval Riphean basins along the joining of the Russian platform plate and the Urals.

DESCRIPTION OF THE MOST IMPORTANT SECTIONS OF THE LOWER RIPHEAN AND THEIR LATERAL VARIATIONS

On the western slope of the Southern Urals, Lower Riphean deposits (the Burzyansk series) occurs within the framework of the Taratashsk and central part of the Yamantau anticlinorium [34, 49].‡

*The advantage of the Riphean stratotype is that it is a component in a number of Riphean basins in the Volga–Urals region, the boundaries, paleogeographies, and source areas of which are fairly accurately reconstructed in contrast to, let us say the Belt.

†In this report, we are including the western slope of the Southern Urals within the composition of the Volga–Urals region. We suggest that the term "Volga–Belyy region" is more suitable than the term "Volga–Urals region" used in the literature (see, for example, [49]).

‡Because the Volga–Belyy region is substantially larger than the western slope of the Southern Urals, most attention in this section will be devoted to a description of the Kyrpinsk series; data on the Burzyansk series is presented in the form of a thesis (it is described most completely in [33]).

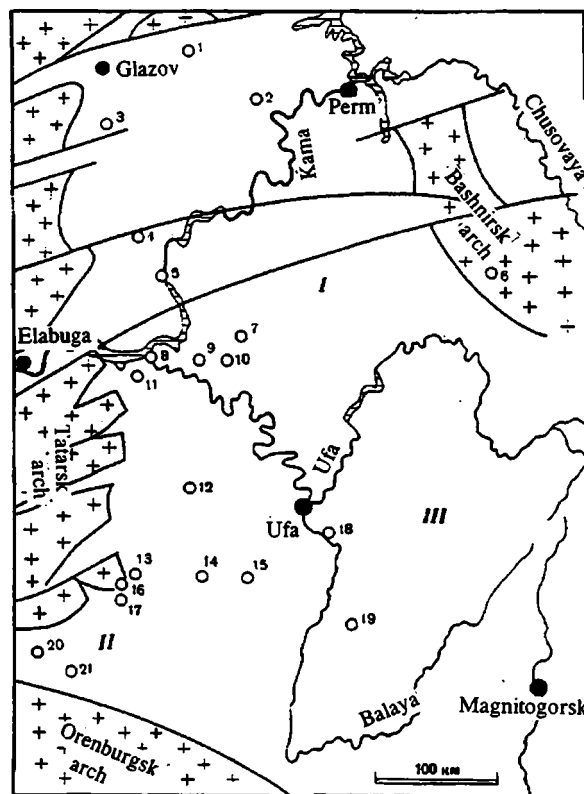


Fig. 1. Locations of principal holes penetrating Lower Riphean deposits in the Kamsk-Bel'sk (I) and Sergiyevsk-Abdullinsk (II) troughs. 1-21) holes (1: Sokolovka-53; 2: Ocher-14; 3: Sektyrka-1201; 4: Izhevsk-20; 5: Sarapul'sk-2; 6: Manchazh-5; 7: Or'ebash-82; 8: Sauzbash-2; 9: Arlan-7000; 10: Nadezhdino-27; 11: Karachevsk-20005; 12: Tyuryushevo-2; 13: Serafimovsk-119; 14: Asly-Kuly-4; 15: Kipchak-1; 16: Urus-Tamak-191; 17: Sulinsk-20 007; 18: Kabakovo-62; 19: Kulgunino-1; 20: Krasnoyarka-35; 21: Sultangulovo-102); III) Bashir meganticlinorium.

The Aysk suite consists of a variegated complex of terrigenous, volcanogenic, and volcanogenic-sedimentary rocks. Within the boundaries of the Taratashk ridge of the Archean-Early Proterozoic, it can be subdivided into two different sequences [30]. The lower sequence includes sandstone, gravellite, conglomerate, trachybasalt, tuffstone, and tuff-breccia of basic composition. The upper sequence is predominantly composed of dark clayey and carbonaceous-clay shales with sparse interbeds of siltstone, fine-grained sandstone, and dolomite with a terrigenous admixture. Southwest of the Taratashk massif, in the basin of the submeridionally running Ay River, the section of the suite is somewhat differently constructed. * Garan' breaks the suite into four subsuites: the Lipovsk, Chudinsk, Kisegansk, and Sungursk. The Lipovsk subsuite is primarily composed of arkosic sandstone with interbeds of siltstone and gravellites. The Chudinsk encompasses clay shale, siltstone, sandstone, and pebble-cobble conglomerate typically forming large lenses in the sections. The Kisegansk and Sungursk subsuites are almost exclusively composed of carbonaceous-clay shales with sparse, thin interbeds of siltstone and sandstone. The total thickness of the suite varies from 1700 to 2200 m [49].

The Satkinsk suite is predominantly composed of carbonate (~85%) chemogenic and phytogenic rocks; packets of members of clayey or carbonaceous-clay shales play a subordinant role in its composition [34]. The total thickness of the suite is estimated as 3000-3500 m [5].

*In this area, the base of the Aysk suite has not been penetrated, whereas, along the periphery of the Taratashk massif, the Aysk suite overlies Archean-Early Proterozoic metamorphites with a sharp unconformity.

The Bakal'sk suite includes clayey and carbonaceous-clay shale, dolomite, calcareous dolomite, limestone, and, in subordinant quantities, phytogenic carbonate rocks and siltstone. Its total thickness is approximately 1400-1550 m [49]. Of this, $\approx$ 450-650 m belongs to the lower (Marakarovsk) subsuite, primarily represented by dark shales with thin interlayers of siltstone and argillaceous limestone. The upper subsuite is an alternation of carbonate and terrigenous packets. To the east and south-east of the Bakal ore field, carbonate packets gradually pinch out, and the eastern sections of the suite are composed of fine-grained sandstone alternating with shales of various compositions [49].

The Bol'sheinzersk suite primarily consists of fine- and intermediate-grained sandstones. Carbonaceous-clay shales (mainly characteristic of the lower and middle parts of the suite), siltstone, and carbonate rock play are subordinate role. The total thickness of the suite is $\approx$ 2200 m [34].

The Suransk suite is divided into five subsuites. The lower and upper subsuites consist of carbonate rocks. Clay-carbonate, clay, and carbonaceous-clay shales, siltstones, dolomites, and their marly varieties play a major role in the middle part of the suite. Limestones (frequently with a terrigenous admixture), sandstones, and phytogenic carbonate rocks are less abundant. The thickness of the suite is estimated to be 1000-2800 m [34].

The Yushinsk suite completes the section of the Lower Riphean in the Yamantau anticlinorium. It is primarily composed of clay and carbonaceous-clay shales occurring both in the form of uniformly constructed packets and within the compositions of packets and members interbedded with siltstone and (or) sandstone. The thickness of the suite varies from 700 to 1100 m.

In the eastern Russian plate, Lower Riphean deposits (the Kyrpinsk series) fills the Kamsk-Belyy (KBT) and Sergiyevsk-Abdullinsk (SAT) troughs. Using deep-drilling and geophysical data, they can be directly traced to the Skladchatyy Urals [44, 49], where they are replaced by formations of the Burzyansk series. The Kyrpinsk series includes the Prikamsk, Kaltasinsk, Nadezhdinsk, and Kabakovsk suites.* The Prikamsk suite can be compared with the Aysk and Bol'sheinzersk suites; the Kaltasinsk with the Satkinsk and Suransk; and the Nadezhinsk and Kabakovsk suites correlate with the Bakal'sk (Yushinsk).

The Prikamsk suite in the southwestern part of the KBT is represented by variegated terrigenous rocks. It is divided into four subsuites [23, 36]: the Azykul'sk, Nortkinsk, Rotkovsk, and Minayevsk. The Azykul'sk subsuite includes brownish-violet, greyish-rosy, and reddish-grey massive or indistinctly banded arkosic and feldspathic-quartzitic sandstone. In the Prizaboy part of the Menzelino-Aktanysh-203 hole, there are amygdaloidal diabasic porphyrites with tuffs of basic composition among sandstones [49]. The origin of these formations is unclear. The Nortkinsk subsuite is composed of variegated siltstone, mudstone, and sandstone, with sparse interbeds of dolomite. The Rotkovsk subsuite is represented by arkosic and subarkosic variegated sandstones with thin interlayers of siltstone. The Minayevsk subsuite includes variegated sandstone, siltstone, mudstone, dolomite, and dolomitic marl. Among the sandstones, there are lenses of gravellite and pebble conglomerate. The total thickness of the suite is more than 1000 m [36].

In the Bavlinsk-Baltayevsk graben, according to L. D. Ozhiganova, the probable analogs of the Rotkovsk and Minayevsk subsuites are the Troitskaya and Mizgirevsk suites respectively. In the section of the Podgornaya-200006 hole, the Troitskaya suite is represented by variegated sandstone with interbeds of subordinant siltstone and gravellite. The Mizgirevsk suite is primarily composed of siltstone and mudstone, with interbeds and micropackets of inequigranular sandstone, dolomite, and gravellite.

In the Tyuryushevo-2 hole, the level under discussion includes two strata previously identified as under the name of the Tyuryushevsk suite [49]. The lower stratum includes reddish sandstone, coarse-grained and poorly sorted. The upper stratum is composed of sandstone interbedded with siltstone and mudstone. It is difficult to correlate this section with the type section of the Prikamsk suite at the Arlan-7000 hole [36].

At the western border of the KBT, at the latitude of Elabuga, the Prikamsk suite is represented by two sequences, according to the data of L. D. Ozhiganova and M. V. Isherska. In the lower part of the section, packets and members of a variously ordered alternation of siltstones, mudstones, and sandstones predominate; in the upper part of the section,

*Since the mid-nineteen sixties, the Kyrpinsk series has been traditionally thought to include the Tyuryushevsk, Arlansk, Kaltasinsk, and Nadzhinsk suites [46, 47, 49]. In recent years, it has been shown that the Arlansk suite in the strato-type section approximately corresponds to the middle part of the Kaltasinsk suite and that the structure of the pre-Kaltasinsk part of the series is more complex than would be expected from the type section of the Tyuryushevsk suite at the Tyuryusevo-2 hole [51]. Because of this, L. D. Ozhiganova has proposed that all terrigenous pre-Kaltasinsk deposits within the Kyrpinsk series can be assigned to a separate, Prikamsk suite.

one finds primarily variegated siltstone and inequigranular sandstone with subordinant interbeds of siltstone, shale, and gravellite. In the Prizaboy part of the Karachevsk-20005 hole, a thick diabase sill has been penetrated.

According to data presented in [28], sandstone, conglomerates of various granulometric classes, gravellite, and breccias predominate in sections of the pre-Kaltasinsk level; they tend to occur toward the Klimkovsk, Nemsk, and Komi-Permyatsk ridges of the basement (the northwest KBT). Siltstone and mudstone play a substantially lesser role.

In the Sarapul'sk graben, pre-Kaltasinsk formations are represented by medium- and coarse-grained variegated sandstones, often with gravel material [55]. Southwest of Sarapul, in the Kuchukovsk area, there are effusives of basic composition among sandstones at the level under discussion [49]. In the near-border part of the KBT (the Sektyrka-1201 and Kosinskaya-460 holes, the Chyrashursk group, etc.), sandstones of various granulometry, with rose-gray, cherry-red, light-gray, and brown colors, predominate at this level. To the east, in the section of the Ocher-14 Hole, L. D. Ozhiganova and M. V. Isherska, discovered analogs of the Rotkovsk and Minayevsk subsuites. The first is primarily composed of sandstone and interbedded packets of sandstone, siltstones, and mudstone; the second includes variegated siltstone (predominating), mudstone, and dolomite with a terrigenous admixture.

East of Glazov and southwest of Siva, pre-Kaltasinsk deposits also consist of variegated inequigranular sandstone. Thus, there are sparse-pebble conglomerate, gravellite, and inequigranular variegated sandstones in their lower parts in the Kulinginsk area [55]. Above, they are succeeded by poorly sorted sandstone. At this level, in the section of the Sokolovka-53 Hole, one can also distinguish two sequences. The lower is composed of gravellite and coarse-grained sandstone. In its upper reaches, sandstone is interstratified with siltstone and mudstone. The upper sequence includes intermediate- and fine-grained sandstone and siltstone with subordinate amounts of mudstone. In the opinion of L. D. Ozhiganova, this sandstone is comparable to the Rotkovsk subsuite of the type section.

In the zone joining KBT and SAT, the Borovsk suite correlates with the Prikamsk suite [42, 49, etc.]. In the axial part of the SAT, the Borovsk suite is predominantly composed of fine- and intermediate-grained, more rarely coarse-grained, sandstone and gravelly varieties of sandstone. According to data presented in [16], the suite is represented by sandstone with interbeds of siltstone, mudstone, and, occasionally, gravellite in the Borovsk area east-northeast of Elkhovka. In the Krasnoyarsk area in the Buguruslan region, coarsely-fragmental formations are also lacking. On the other hand, near-boundary sections of the Borovsk suite (the Elkhovsk, Sernovodsk, Gor'kovvrazhnaya, Sultangulovsk areas, etc.), are characterized by a predominance of coarsely fragmental rock, including coarse-grained gravelly sandstone, gravellite, and conglomerate [2, 15, 16, 42].

The Kaltasinsk suite is represented by pelitomorphic chemogenic dolomite; phytogenic and clastic varieties of dolomites play a lesser role in its section. Terrigenous and terrigenous-carbonate formations, including clayey limestone, marl, shales of various compositions, and siltstone play an important role in the middle part of the suite in a number of sections. This allows us to divide the suite into three subsuites (from bottom to top): the Sauzovsk, Arlansk, and Ashitsk [36]. The Sauzovsk subsuite is represented by gray, rose, and greenish-gray, predominantly massive, dolomites, including stromatolitic varieties. There are dark-gray mudstones in the form of thin but frequently occurring interlayers among dolomites. Siltstones are also found in some intervals. The Arlansk subsuite includes gray, dark-gray, and greenish-gray argillaceous limestone, variously tinted mudstone, siltstone, dolomite, and marl. The Ashitsk subsuite is composed of light- and dark-gray massive dolomite with thin interlayers of limestone and fine-grained terrigenous rock. According to the findings of Frolovich [53], rocks of the Kaltasinsk suite are found over almost all of the KBT.

Analysis of structural and compositional variations of the Kaltasinsk level within the territory of the KBT is substantially impeded by erosion of the roof of the Kaltasinsk suite and the absence of overlying sections in many areas.

West of Arlan, the Sauzbash-2 Hole apparently penetrates only the lower and middle parts of the Sauzovsk subsuite [23], it is predominantly represented by chemogenic dolomite. According to the findings of Ozhiganov, once again only the Sauzovsk subsuite was preserved from pre-Vendian erosion south of Arlan, in the Ik-Bazinsk area; here, the subsuite is primarily composed of dolomite and dolomitic marl, with interbeds of clay shales in the lower and upper parts. To the east, the three-member structure of the Kaltasinsk suite is well expressed in holes in the Or'ebashsk area.

In the Bavlinsk-Baltayevsk graben, according to the data presented in [36], the analog of the Sauzovsk subsuite is probably the Malokamyshsk suite, represented by variegated dolomite within interlayers of sandstone and siltstone containing glauconite [49]. A remarkable feature of this part of the KBT is the abrupt reduction in the thicknesses of the Kaltasinsk suite and its analogs. In the Asly-Kul'sk area to the east, only the Arlansk and Ashitsk subsuites have been penetrated, and the top of the latter has been thinned by pre-Middle-Riphean erosion. According to the findings of Isherskaya [23], the Arlansk subsuite is composed here of an interbedding of dolomite, occasionally with stromatoliths,

mudstone, and marl, whereas the Ashitsk subsuite is primarily composed of dolomite with sparse interbeds of limestone and mudstone.

At the approximate latitude of Sarapul, the Manchazh-5 Hole penetrates the section of the Kaltsinsk suite characterizing the eastern border of the KBT [20]. A typical feature of this suite is an alternation of fairly thick packets of essentially dolomite and interbedded packets with siltstone and mudstone.

In the more northwesterly areas of the KBT, this level shows a somewhat different structure, as is very evident at the Izhevsk-20 Hole. The Kaltasinsk suite has been divided into six strata on the basis of lithological features and geophysical data [55].* As is typical of the more southerly areas, the terrigenous horizon in the middle part of the suite is wedged out by a stratum of dark-gray limestone with interbeds of argillaceous limestone.

To the east, the suite is again incompletely represented. At the Kiyengop-1 Hole, the southern part of the section includes dark-gray dolomite with a brownish tint, black dolomite, and interbeds with a brecciform structure. Upward, we find green siltstone, sandstone, and mudstone alternating with one another and succeeded by variegated dolomite with packets of gray varieties containing interbeds of brownish mudstones.

In the Ocher area (Hole 14) to the north of the KBT, only the Sauzovsk subsuite, consisting of gray, dark gray, and brownish-gray, dolomite and limestone, dolomitic marl, and dolomitized limestone, has been preserved from pre-Vendian erosion.

The Nadezhdinsk suite is represented by a fine alternation of variegated mudstone, clayey siltstone, and marl of dolomitic composition [47, 49]. In the majority of known sections, it is cut by numerous dikes of basic composition. According to the findings of Isherskaya [23], two subsuites can be differentiated within the suite. The lower subsuite is primarily represented by sandstone with thin interlayers of gravellite, siltstone, and, occasionally, mudstone (the color of the rock is variegated gray- and lilac-rose, brownish-gray). The upper subsuite is represented by siltstone, mudstone, marl, and dolomite.

In the type section south-southeast of Sarapul, the suite is represented by variegated mudstone, reddish-brown and greenish-gray feldspathic-quartzitic siltstone and sandstone. Often, one can find thin interlayers of dolomite [46, 51]. Two of the three intervals belonging to the Nadezhdinsk suite come up against a gabbro-diabase dike here.

At the Or'ebash-83 Hole to the northeast, a packet of thin, frequently lenticular interbedding of violet-reddish-brown mudstone, argillaceous siltstone, and marl are found at the Nadezhdinsk level [47]. The upper part of the packet, as at the Nadezhdino-2 Hole, is cut by a diabase dike.

In the central part of the KBT, at the latitude of Sarapul, the suite is primarily composed of siltstone lying above typical Kaltasinsk argillaceous dolomite and below sandstone of the Gozhansk suite of the Vendian [2].

At the juncture of the SAT and KBT, the Nadezhdinsk suite is represented in its lower part by greenish- and rose-gray fine- and intermediate-grained sandstones containing interlayers of mudstone in subordinate quantity. The upper part of the suite is represented by variegated and reddish mudstone with interbeds of siltstone and dolomitic marl [45]. To the south and east, the structure of the suite is approximately the same. The very lowest, sandy-clayey stratum (the interval of 3641.6-3645.2 m) probably corresponds to the Minayevsk subsuite of the Prikamsk suite.

In the center of the southern part of the KBT, analogs of deposits of the Nadezhdinsk suite include formations of the Kabakovsk suite penetrated northwest of Sterlitamak (the Kipchak-I Hole) and 30 km southeast of Ufa (the Kabakovo-62 Hole) [3]; these are dark-colored carbonaceous mudstones in a fine alternation with siltstones.

Finally, the Kulgunino-I Hole, located at approximately the same latitude but already within the Bashkir meganticlinorium (BMA) penetrates deposits of the Yushinsk level; these deposits are variously sequenced and variously sized alternations of siltstone and carbonaceous mudstone [3].

EARLIER CONCEPTIONS OF DEPOSITIONAL ENVIRONMENTS OF THE LOWER RIPHEAN DEPOSITS OF THE VOLGA-URALS REGION

Reconstructions of depositional environments of Riphean complexes of the Southern Urals and the Volga-Belyy region have traditionally shown a few points of agreement.

*The lowest, sandy silty stratum (the interval of 3641.6-3645.2 m) probably corresponds to the Minayevsk subsuite of the Prikamsk suite.

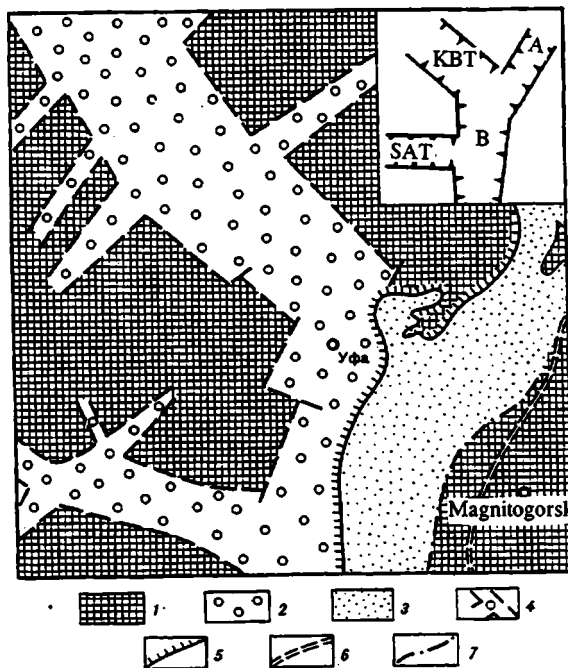


Fig. 2. Map of structural-tectonic regionation of the Southern Urals and eastern areas of the Russian platform during the Early Riphean (according to [40]): 1) platform basement; 2) sedimentary complexes; 3) volcanogenic-sedimentary deposits; 4) tectonic boundaries of the KBT and SAT; 5) present-day western boundary of the Skladchaty Urals; 6) Glavnny Ural'sk abyssal fault; 7) Kiryabinsk-Krakinsk abyssal fault; A) Aysk graben; B) Bashkir graben.

The opinion of most investigators is that the terrigenous deposits of the Prikamsk (the Tyuryushevsk and Borovsk) suites are primarily represented by continental formations [16, 22, 42, 54]. Among these formations, one can find relicts of displaced zones of weathering, avalanche, near-slope, alluvial, and lacustrine sediments, as well as deposits of transient streams [22, 54]. According to data presented in [2], in the more westerly areas of KBT, the Tyuryushevsk suite is primarily represented by eluvial-deluvial deposits which are succeeded in an easterly direction by nearshore and nearshore-marine formations. A similar trend is characteristic of deposits of the Borovsk suite in the SAT [16]. L. Z. Egorova, when describing the land surrounding this trough at the beginning of the Riphean, notes that the trough was probably bordered from the south by a mountain ridge, whereas a fairly gentle plain existed to the north. It has also been hypothesized that the deposits of the Borovsk suite accumulated in a trough of the intermontaine-basin type, where jointly merging alluvial fans merging formed along the periphery and were succeeded in a distal direction by essentially alluvial complexes [2].

Continental depositional environments have been reconstructed for the lower part of the Aysk suite in recent years [30, 32, 34, 39, 41]; these reports describe eluvial, eluvial-deluvial, alluvial, and nearshore-continental deposits and deposits of piedmont belts. Nearshore-marine terrigenous and carbonate deposits play subordinate roles here [32]. At the time of formation of deposits in the lower part of the Aysk suite, the source area was one of fairly dissected relief and was located in direct proximity to the sedimentation basin. Garan' [10] referred to this area as the "Eastern Karelides," and Olli has referred to it as the "Iotnides of the pre-Urals." The latter, according to Olli, were located within the present-day Urals region [37, p. 378]. The upper of the section at the Aysk level is represented by a complex of deposits of different origin [32]. These are lacustrine-marine [41] or essentially marine complexes distant from the shore [32, 34]. Deposits of the Bol'sheinzersk suite which are synchronous with the Aysk suite include moderately-deep water terrigenous sediments formed as a result of the action of density currents [32] and, to a lesser degree, shallow water-marine, terrigenous, and carbonate formations.

Deposits of the Kaltasinsk suite are of shallow water-marine or marine origin [21, 29, 42, 48, 51], although the presence of clastic dolomite at various levels of the section allows us to assume repeated drainage and erosion of individual areas of the basin floor [20] or the existence of ephemeral islands [29]. In the opinion of I. E. Postnikova, an extensive

marine transgression coincided with the beginning of the Kaltasinskian; resulting, during its maximum phase, in the formation of an uncompensated basin in the center of the KBT, a basin where argillaceous carbonate depression facies accumulated. To the west and east, this basin was rimmed with reef masses [29, 42].

For the Satkinsk-Suransk level of the stratotype section, we can also assume predominantly shallow water-marine and marine origins for the deposits [5, 10-12, 30, 32, 34], among which we can recognize carbonate and terrigenous sediments of nearshore submarine, unrestrictedly moving and poorly moving shallow water, as well as formations far from coastal zones and lagoonal-marine complexes.

Deposits of the Yushinsk and Bakal'sk suites have roughly the same origin [26, 27, 30, 32, 34]; for the latter, sediments of littoral zones can be reconstructed in a number of cases.

A summary model of the evolution of the Early Riphean basin in the northeast of the BMA has been proposed by Anfimov [4].

According to his data, deposits in the lower part of the Burzyansk series accumulated under continental conditions within a narrow grabenlike trough; the middle and upper levels of the series consist of marine carbonate and carbonate-clay formations.

At the end of the 1970s, the emergence of theories concerning riftogenic depression-related evolution of the Urals crust during the Riphean [17-19, etc.] led not only to a reassessment of views on the history of development of sedimentation basins in the Urals and the eastern part of the Russian plate [1, 24, 38, 39, etc.], but also to the first reconstructions which treated these two regions as one. According to the data of Axsenov and Solontsov [1], the Kamsk-Belyy northwest striking rift system was in existence at the beginning of the Early Riphean. During the initial stages of its development, fine-grained alluvial and lacustrine deposits of the lower part of the Prikamsk suite formed in gently inclined basins. During the second half of the Prikamskian, rates of downwarping and differential movement of blocks sharply increased and dissected relief formed in the source area. This promoted deposition of predominantly coarsely fragmental terrigenous formations.* The third stage (the Kaltasinskian) was characterized by transgression of a shallow water-marine basin with increasing regressive trends at the end of the Kaltasinskian and during the Nadezhdinskian. The clearest conceptions of the unity of the KBT, SAT and Bashkirsk troughs during the Early Riphean have been presented in the writings of Parnachev [38-40, etc.]. In his view, domelike uplift of a basement with dissected mountainous topography and a number of small grabens took place in the territory under consideration by the beginning of the Riphean. During early Ayskian time, a complex rift system reminiscent of a typical "triple articulation" formed. According to V. P. Parnacheva, this rift system included the Kamsk-Bel'sk, Aysk and Bashkirsk grabens filled with coarsely fragmental molassoids (Fig. 2). Subsequently, rates of downwarping declined, graben structures disappeared, and predominantly shallow water-marine terrigenous and carbonate sedimentation died down. A comparison of a number of Riphean formations in the grabens described strongly suggests that the Riphean system evolved according to a unified pattern [41]. It is interesting, however, that whereas an essentially riftogenic stage lasted to the beginning of Ayskian time in the type section of the Riphean [32, 34], it extended to the end of the Prikamskian in the east of the Russian plate [1].

COMPLEXES OF DEPOSITS OF DIFFERENT COMPOSITIONS AND ORIGINS AND THEIR DISTRIBUTIONS WITHIN SECTIONS OF THE LOWER RIPLEAN

Examination of the textural features of rocks in the stratotype section of the Riphean [32, 34] and Upper Precambrian deposits of the Volga-Belyy region in a number of the most representative holes, investigation of the structural patterns of the suites, and consideration of published data allows us to distinguish a number of large-scale complexes of deposits of various origins and compositions. Analysis of lateral and vertical interrelations between complex in sections of series makes it possible to construct schematic lithological-paleogeographic maps and reconstruct the history of the Early Riphean sedimentation basin in broad outline.

Among terrigenous deposits, the following complexes can be identified.

*It should be emphasized that the sequence of events described has been widely adopted in two-stage models of the formation of Cenozoic rifts [9, 13, 31].

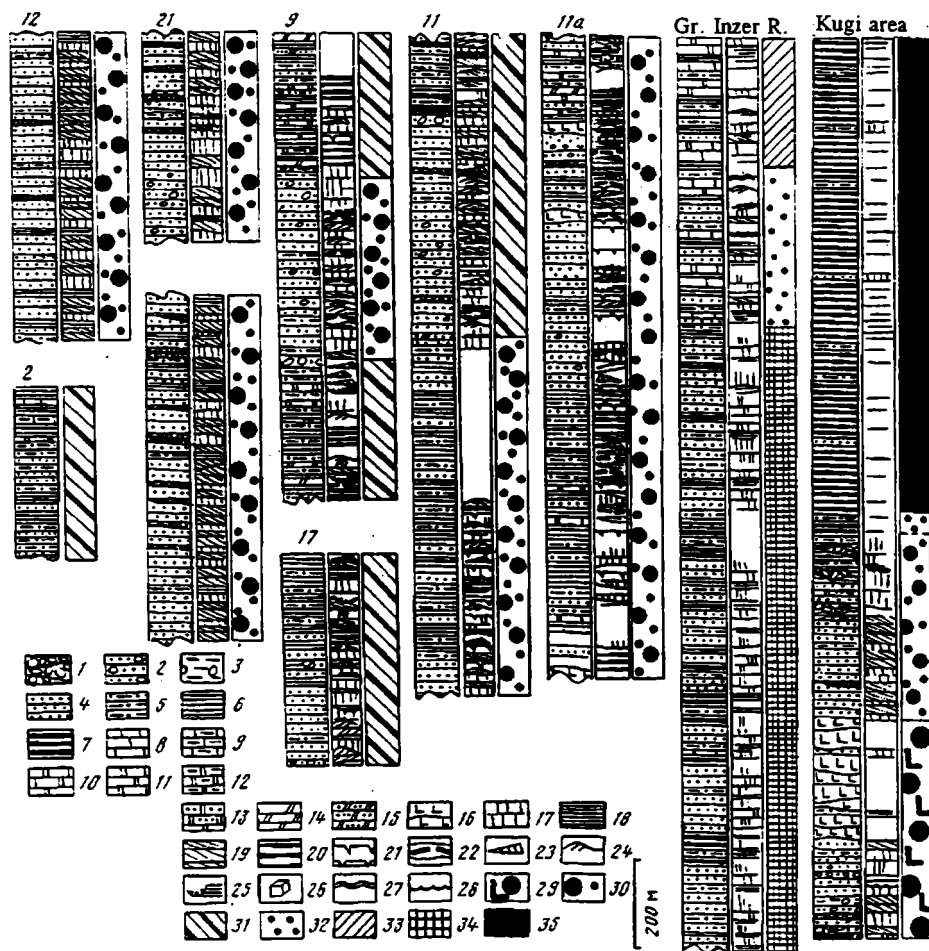


Fig. 3. Structure of sections, textural features of deposits and sedimentary complexes at the Aysk-Prikamsk level of the Lower Riphean in the Volga – Urals region (the number of a section corresponds to the number of the hole in Fig. 1): 1-16) lithological rock types (1: conglomerate and gravellite; 2: sparse-pebble sandstone; 3: clay shale with pebbles; 8: limestone; 9: argillaceous limestone; 10: calcareous dolomite; 11: dolomite; 12: argillaceous dolomite; 13: dolomite with terrigenous admixture; 14: dolomitic marl; 15: same, with terrigenous admixture; 16: diabase); 17-28) textural features of rock (17: massive unstratified intervals; 18: horizontal layering; 19: cross-stratification at various scales; 20: gently wavelike interbedding of various lithological rock types; 21: dessication cracks, 22: tabular breccia of clay shales; 23: intervals with ripple marks, 24: cross wavelike lamination; 25: micro-faults and washouts; 26: crystal molds from halite crystals; 27: symmetrical sinusoidal undulation ripple; 28: also sharply crested); 29-35) sedimentary complexes (29: volcanogenic-terrigenous, predominantly continental deposits; 30: ??? 31: littoral ("extremely shallow-water") terrigenous formations; 32: shallow water-marine terrigenous deposits; 33) terrigenous-carbonate deposits of shallow water-marine origin; 34: terrigenous, moderately deep-water formations; 35) terrigenous sediments with soluble organic matter located far from shore).

A complex of volcanogenic-terrigenous, predominantly continental and nearshore-continental deposits is represented by conglomerate, gravellite, and sandstones of polymictic and arkosic compositions alternating with sheets of trachybasalt. Sedimentary rocks show several types of cross-lamination, numerous dessication cracks, washouts, ripple marks, etc. In addition to uniform packets, there are packets and interbedded members of sandstone, siltstone, and clay shale with dessication cracks. A detailed lithological-facial analysis reveals that deposits of a given complex may contain fluvial, flood-plain, nearshore, bay-lagoon, proluvial, and other facies of similar depositional environments [34, 41]. This complex is characteristic of the lower three subsuites of the Aysk suite (Fig. 3); a detailed description of it is presented in [32].

A complex of terrigenous sediments of predominantly continental and "extremely shallow-water" origin is clearly segregated within sections of the Prikamsk suite.* Here, it is primarily represented by variegated fine-, intermediate-, and coarse-grained sandstones. Siltstone, gravellite, and packets of thin, gently wavy, interbedded siltstone and shale are present to a significantly lesser degree within its composition. As a rule, the sandstones are reddish-grey, rosy, rosy- and greenish-grey and show, at different scales, cross-lamination, wavelike lamination, gentle wavelike lamination, numerous dessication cracks, and intervals of tabular breccia. Massive and indistinctly and finely banded varieties of psammites are widely occurring. Packets of gentle wavelike interbeddings of siltstone and shale alternating with sandstone are characterized by widely occurring dessication cracks, lenticular-cross-lamination and cross wavelike lamination. The most typical representatives of deposits of this complex are rocks of the Rostkovsk subsuite of the Prikamsk suite at the Arlan-7000 hole and the Borovsk suite in the near-border part of the SAT (see Fig. 3).

A complex of terrigenous deposits of nearshore-basin origin includes fine-, intermediate-, and coarse-grained variegated sandstones in association with siltstone, mudstone, and, occasionally, dolomite (Fig. 4). The latter are typical of a number of sections of the Nadezhdinsk suite (Asly-Kul'-4, etc.). The rocks of this complex are violet, cherry-red, rose-grey, light-rose or brick-red and show a broad spectrum of structures: horizontal, undulatory, and steeply dipping cross-stratification at various scales, cross wavelike, wavelike, and lenticular lamination, small faults and erosion channels. Frequently, one finds cherry-red and chocolate silty clay shales emphasized by gentle wavelike and wavelike lamination in the form of gentle wavelike interlayers among sandstone. In contrast to the complex described earlier, these formations do not show many textures-indicators of periodic dessication of sediments; this allows us to consider them as predominantly basinal, although nearshore, deposits. They are typical of the Norkinsk and Minayevsk subsuites of the Prikamsk suite in the section of the Arlan-7000 hole, the Rotkovsk subsuite at the same level in the Menzelino-Aktanysh-20005 hole, and also the Nadezhinsk suite. In the Burzyaniye type section, their role is minor [26, 27].

Terrigenous shallow-water marine formations, on the other hand, are more typical of sections of the BMA, where they are known to occur at the Bakal'sk (Yushinsk) level. These are packets and members with gentle wavelike alternation of clay and carbonaceous-clay shales, siltstone, and (or) fine-grained sandstone with diverse flow structures, including fine cross-lamination, cross wavelike lamination, current ripple marks, primary flow lineations, etc. There are no dessication cracks, erosion-channel or fault structures among the deposits of this complex. As a rule, the stratification is marked by thin interlayers and interstratified beds of dark siltstone and silty clayey shales.

A complex of terrigenous sediments distal to the shore includes three varieties. The first is represented by dark finely layered, horizontally layered, or massive clay shales with sparse, thin interlayers of siltstone and carbonate rock. These formations are characteristic of the Makarovsk level of the Bakal'sk suite as well as the Kisegansk and Sungursk subsuites of the Aysk suite, and occur in sections of the Kabakovsk suite. The predominantly pelitic dimensions of the terrigenous material, the almost complete absence flow structure and indications of period dessication suggest deposition of the sediments below wave base at a substantial distance from the shore zone. The second variety includes bluish-green, thinly and uniformly banded shale (fine-grained siltstone) and the Angastaksk subsuite of the Suransk suite [32]. The third variety includes massive textureless sandstone with bimodal structure and thin interlayers of shale and siltstone typical of the lower and middle levels of the Bol'sheinzersk suite. Their formation probably occurred as a result of gravity flows [32] in relatively deepwater parts of the basin.

The complex of terrigenous-carbonate deposits of shallow water-marine origin is most typically represented in sections of the upper subsuite of the Bakal'sk suite, where there is a mesorhythmic alternation of terrigenous and carbonate packets [27, 33, etc.]. Within the composition of the latter, there is a complex marriage of facies, including circum-dome formations of a carbonate platform, lagoonal and nearshore-marine sediments, deposits of nearshore marine shoals, etc. The formation of the entire complexly structured sequence of deposits in the upper part of the Bakal'sk suite took place under shallow-water basinal conditions against a background of alternating open and semi-restricted environments [27, 41]. Deposits in the upper part of the Baolsheinzersk suite probably have a similar origin [32].

Carbonate deposits include two complexes.

The complex of carbonate sediments of shallow-water shallow-water basinal origin is primarily represented by chemogenic dolomite and argillaceous dolomite; other varieties of carbonate rock and clay shales play subordinate roles in its section. The color of the rock is grey and greenish-grey, occasionally with lilac or rosey tints. The most typical

*On the western slope of the Southern Urals, this complex is negligibly thick and does not play an independent role.

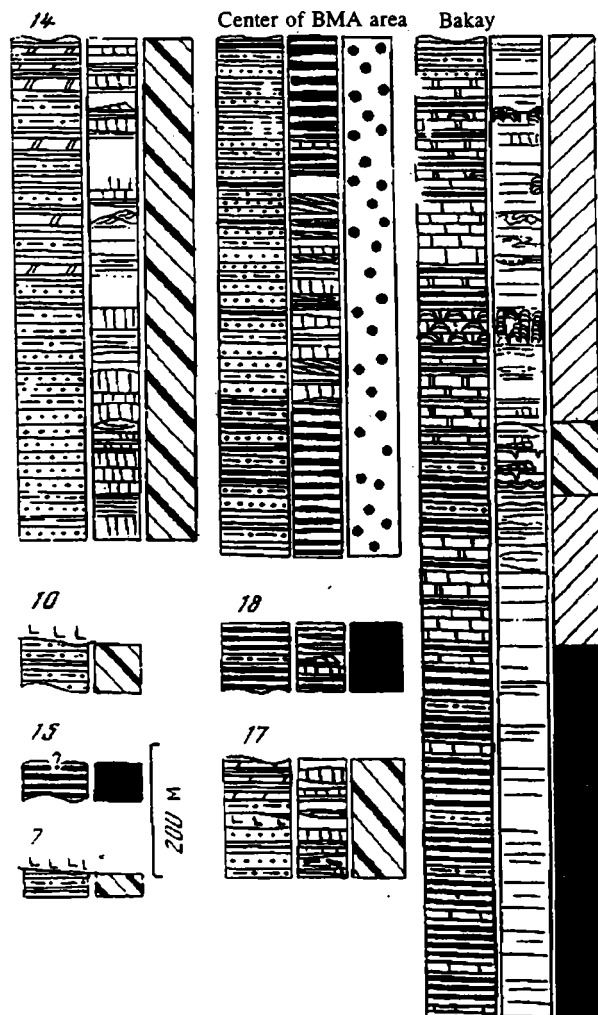


Fig. 4. Structure of sections, textural features, and sedimentary complexes of the Bakal'sk-Nadezhdinsk level in the Volga-Urals region (the number of a section corresponds to the number of the hole in Fig. 1). See Figs. 3 and 5 for explanations of symbols.

structures are indistinct banding, gentle wavelike lamination, compacted interlayers and lenses of flat-scare carbonate breccia, a portion of which consists of tempestites [32] and stromatolitic structures. There are many massive unlayered intervals of dolomite, and, in cases where substantial amounts of terrigenous admixtures are present, gentle wavelike lamination and cross gentle wavelike lamination. Stromatolitic and microphytolithic dolomites form thin beds and packets among chemogenic varieties. Clastic dolomites (brecciated dolomite, etc.) tend to occur in sections of the Kaltasinsk suites toward the north-west [29]. In these regions, there are higher quantities of limestone, clayey, silty-sandy, and sandy varieties of shales. The complex described is typical of most sections of the Kaltasinsk suite (Arlan-7000, Or'ebash-82, Ocher-14, Izhevsk-20, etc.) as well as a number of levels of the Satkinsk suite [32] (Fig. 5).

The complex of carbonate sediments is primarily represented by dolomite, more rarely argillaceous dolomite which is grey (dark or light grey), massive, and thin-banded or indistinctly banded. The lack of noticeable quantities of terrigenous admixtures and flow structures suggests formation of deposits of this type at substantial distances from the source area, in zones of the basin with calm hydrodynamics. Similar formations are characteristic of a number of sections of the Kaltasinsk suite in the north-west, in the axial zone of the KBT, and at several levels of the Satkinsk suite.

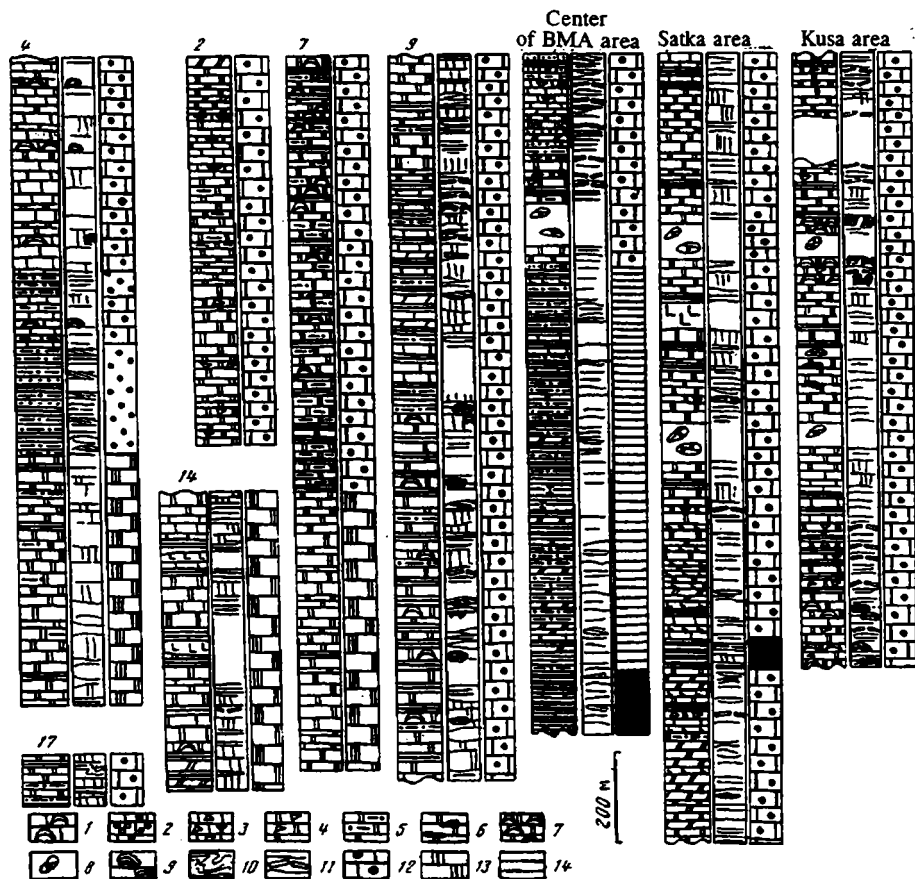


Fig. 5. Structure of sections, textural features of deposits, and sedimentary complexes of the Satkinsk-Kaltasinsk level of the Volga-Urals region (the number of a section corresponds to the number of the hole in Fig. 1). 1-8) lithological rock types (1: stromatolitic limestone; 2: same, microphytolithic; 3: flat-scaree limestone breccia; 4: same in dolomite; 5: dolomite with silty admixture; 6: same with chert nodules; 7: same, stromatolitic; 8: composition of rock from ooze); 9-11) textural features of rock (9: stromatoliths; 10: intervals with convolute layering; 11: intervals of flat-scaree carbonate breccia); 12-14: sedimentary complexes (12: shallow-water marine carbonate formations; 13: essentially marine, basinal deposits; 14: fine-grained terrigenous sediments of distal zones). For other symbols, see Fig. 3.

PALEOGEOGRAPHY OF THE EARLY RIPHEAN VOLGA-URALS SEDIMENTATION BASIN

Despite a fairly large amount of geological data on the Upper Precambrian complexes of the Volga-Urals region, almost no lithological-paleogeographic maps which cover the Tatarstan, Bashkortostan, Perm', Orenburg and Samara regions of Russia have been produced thus far. Exceptions include small-scale maps [6] showing the evolution of the environment at the level of sedimentary series and unpublished lithofacial maps by L. D. Ozhiganova and M. V. Isherska (1977),* for the Upper Riphean and Vendian of the eastern Russian plate and the BMA, and also the maps by Yu. R. Bekker for the Vendian [7]. For the Lower Riphean, the similar situation can be explained, for the most part, by the low degree to which the sedimentary complexes in the central, most buried zones of the KBT have been studied, although the general aspects of the evolution of the Early Riphean basin could be established now by means of an analysis of lithological-paleogeographic maps compiled from studies of lateral interrelations between the above-described complexes of deposits for the "beginning" and "end" of the Ayskian-Prikamskian, Satkinskian-Kaltasinskian, and Bakal'skian-

*This map series has the most detailed coverage of stratigraphic levels. Maps were compiled for subsuites of the Zil'merdak'sk suite and formations correlating with it on the platform, as well as for the Katavsk, Inzersk, and Min'yarsk suites of the Upper Riphean and all four suites of the Southern-Urals Vendian.

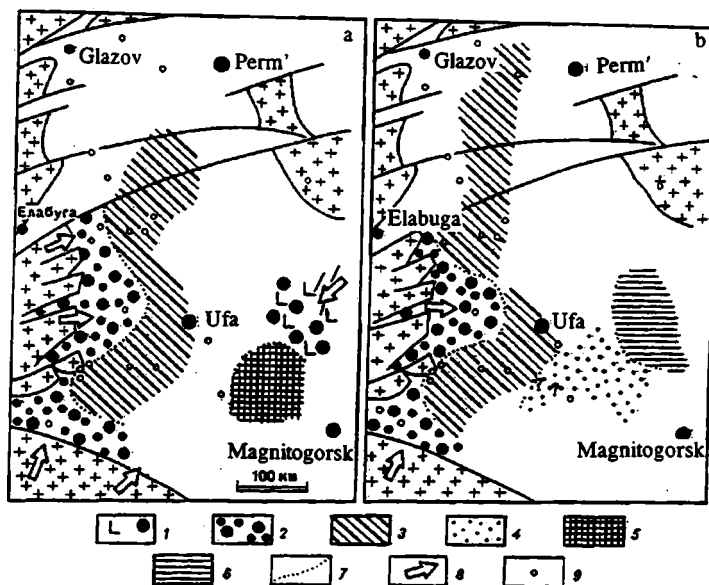


Fig. 6. Schematic lithological-paleogeographic map of the Volga-Urals region for the beginning (a) and end (b) of the Ayskian-Prikamskian: 1) region with predominance of volcanogenic and terrigenous continental formations; 2-6) same, terrigene (2: continental, 3: littoral - "extremely shallow-water"; 4: shallow water-marine; 5: moderately deepwater; 6: fine-grained); 7) boundaries of paleogeographic zones; 8) directions of supply of detrital material; 9) locations of holes.

Nadezhdinskian. In the case of levels which are strongly differentiated in terms of lithology (the Ayskian, Bakal'skian, etc.), this would reveal variations in paleogeographic environments in more detail.

The Aysk-Prikamsk Level. At the beginning of the Ayskian-Prikamskian, a number of zones became established along the periphery of the basin (Fig. 6a). For the most part, these were zones of predominantly continental (alluvial, deluvial-proluvial, etc.) pebbly-gravelly-sandy and sandy-silty sediments tending to occur in the regions of Kinel, Bugurslan, Bavlov, Elabuga, etc., i.e., toward the southern periphery of the KBT. The textural features of the rocks and the "organization" of lithological and genetic types of sediments within sections of this zone suggest that the formation of the deposits took place as a result of the activity of several branching (many-armed) rivers carrying detrital material both from a moderately uplifted and dissected land area (the vicinity of the present-day SAT) and from regions of gently rolling topography (the eastern Russian plate).

To the east, lay a zone of predominantly nearshore-continental and nearshore deposits extending from the Sarapul area to the latitude of Ufa and further to the southwest, to Urus-Tamak. This zone was probably an extensive littoral (playa?) region, since the sediments here show, in addition to their variegated reddish coloration, widespread dessication cracks of various sizes and morphology in association with ripple marks of waves and currents, fine cross wavelike lamination and similar textures.

To the southeast, along the periphery of the Taratashsk massif, a composite complex of terrigene deposits alternating with flows and sheets of trachybasalt was formed; this complex probably marks the "riftogenic" border of the trough. The presence of numerous lenses and interlayers of conglomerate here also suggests an active tectonic environment, frequent reorganizations of the structural plan, and dissected topography in the source area. Both crystalline complexes of the Archean-Lower Proterozoic and slightly metamorphosed sedimentary formations of the Iotniysk type served as sources of detrital material (L. V. Anfimov, personal communication, 1992). To the southwest, in the central regions of the BMA, the Aysk-Prikamsk level is mainly represented by moderately deepwater silty-sandy and sandy sediments which probably formed beyond the brow of the outer shelf.

Consequently, it can be assumed that the Early Riphean sedimentation basin, during the very early stages of its development, had a much more asymmetrical structure. Its western, northern, and southwestern flanks were occupied by extensive, fairly built-up alluvial-deltaic, and nearshore-continental plains changing to shallow water-marine landscapes with deposition of predominantly terrigenous sediments to in eastern and southeastern directions. On the one hand, the southeastern border* was a terrain of active tectonic activity and was linked to substantial uplifts (probably bounded by escarpments, benches, or ridges of the basement). Evidence for this also includes a substantial variegation and contrast of facies in sections of the Aysk suite, substantial variations in thicknesses of deposits, and the presence of vulcanites. Analogs of the Aysk suite in the central areas of the BMA (the Bol'sheinzersk suite) consist of mass-flow deposits probably marking a separate area of depression aligned with a narrow shelf zone rimming (?) the Taratashsk ridge of the basement.

The end of Ayskian-Prikamskian times was marked by reorganization of the overall style of sedimentation mainly in the vicinity of the southeastern border (see Fig. 6b). The region of dissected, hilly topography supplying most of the detrital material for volcanogenic-terrigenous complex of the lower part of the Aysk suite was, at this time, completely flattened. There is almost no evidence of former sources of coarsely fragmental terrigenous material over the entire many-hundred-meter section of the Kisegansk and Sungursk subsuites. Deposition of gravity-created formations also ceased within central parts of the BMA and substantial overall flattening of the basin floor probably took place. It is interesting that a regular succession of sedimentary complexes, from alluvial-deltaic through nearshore- and shallow water-basinal probably to essentially basinal can be identified in the upper part of the Aysk-Prikamsk level from the west to the east (in a strip approximately extending from Bavlov to Tolbaz and, further to the northeast, to Kusa). In our view, this suggests substantial broadening of the basin in an eastern direction and onset of a clearly expressed transgression.

The Satkinsk-Kaltasinsk Level. This level is characterized by a sharp predominance of carbonate deposits over almost the entire basin. Only in the southeast (within the central areas of the BMA) do a succession of the most western, northwestern, and eastern sections of the Kaltasinsk suite show wedging out of a uniform multikilometer carbonate sequence by terrigenous, predominantly fine-grained formations. The absence of "transitional" terrigenous-carbonate and terrigenous types of sections stratigraphically comparable to the Kaltasinsk dolomite in the most westerly reaches of the BMA suggests a large-sized basin during the Satkinskian-Kaltasinskian; this assumption is supported by the presence of dolomite "caulking" in rocks of the crystalline basement. The paleogeographic setting at the beginning of the Satkinskian-Kaltasinskian, when a region of essentially basinal carbonate sediments appeared in the central and northwestern parts of the KBT is also suggestive of this (Fig. 7a). To the north and west, it was rimmed by zones of deposition of shallow water-marine dolomite; in the southeast, it probably directly bordered, or was connected through a zone of shallow-water sediments (?), with a zone of "unstable" carbonate deposition, where environments of terrigenous and carbonate deposition alternated over time. This allows us to suggest that the main source of clastics to the basin at the beginning of the Satkinskian-Kaltasinskian was a region lying to the east and southeast of the present-day BMA.†

The end of Satkinskian-Kaltasinskian was marked by ubiquitous predominance of shallow water-marine chemogenic and, in individual regions and zones, phytogenic carbonate sediments (see Fig. 7b). The central area of the BMA emerges again as an exception; this is an area where maximum deposition of a similar type of formation came at the very end of the time interval under consideration, probably coinciding with maximum transgression and tectonic stabilization of the region. During the Satkinskian-Kaltasinskian, the sedimentation basin approximated a flat epicontinental water basin with respect to many parameters.

The Bakal'sk-Nadezhinsk Level. In sections of the Bakal'sk, Yushinsk, Nadezhinsk, and Kabakovsk suites, which are included at this level, there is a predominance of terrigenous deposits of shallow water-basinal and nearshore-basinal origin. Over almost the entire duration of the Bakal'skian-Nadezhinskian, nearshore-continental and nearshore-marine landscapes with deposition of variegated sandy-silty, silty, and silty-clayey sediments predominate on the western flanks of the basin. Deposition of shallow-water-marine terrigenous formations in the central areas of the BMA was fairly steady.

*The southern and northeastern flanks of the basin have not been reconstructed for this time interval.

†Variations in the supply of clastics for individual subsuites of the Suransk suite in the central parts of the BMA were more complex but were probably local nevertheless [33].

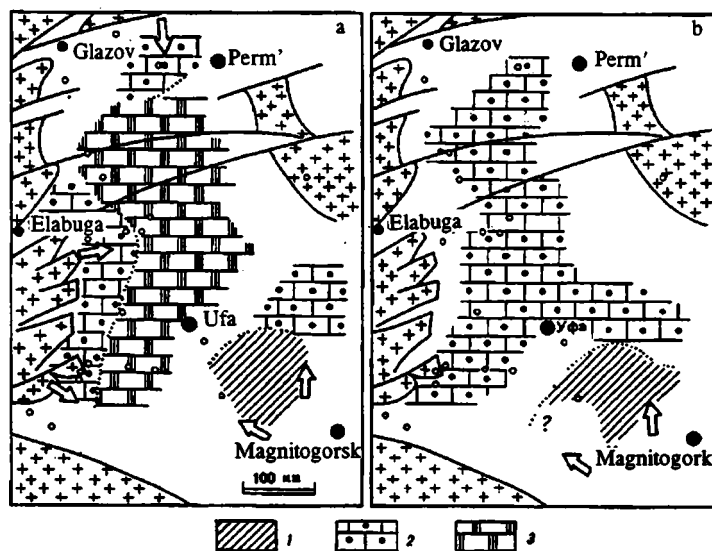


Fig. 7. Schematic lithological-paleogeographic map of the Volga-Urals region for the beginning (a) and end (b) of the Satkinskian-Kaltasinskian: 1) terrigenous-carbonate deposits of shallow water-marine origin; 2) complex of carbonate shallow water-marine deposits; 3) carbonate basinal formations. See Fig. 6 for other symbols.

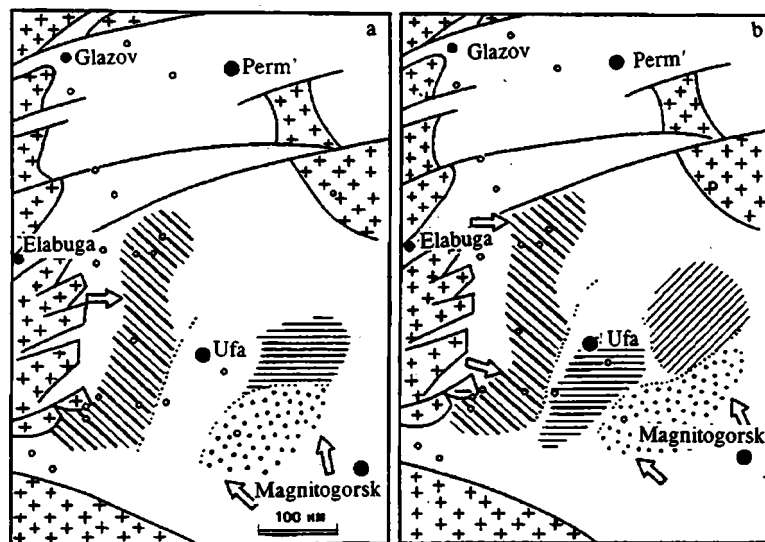


Fig. 8. Schematic lithological-paleogeographic map of the Volga-Urals region for the beginning (a) and end (b) of the Bakal'skian-Nadezhdinskian. See Fig. 7 for other symbols.

The fine-grained terrigenous sediments most remote from the coastal zones probably tended to occur toward the northeastern areas of BMA at the beginning of this time (Fig. 8a), but shifted southwestward, into the center of the basin, at the end. In the southeast direction, the latter were primarily replaced by silty-sandy sediments of shallow water-basinal origin; the zone of distribution of these sediments extended into the central areas of the present-day BMA.*

*Substantial erosion of deposits at this level within the KBT and SAT hinders reconstruction of a more complete map of the distribution and evolution of landscapes of Bakal'skian-Nadezhinskian time.

It should be noted that a zonation approaching the symmetrical clearly emerged in the basin during the Bakal'skian-Nadezhinskian. The eastern regions of the Russian plate and regions located south-east of the present-day BMA emerged as sources of washdown. Both these and other areas already had been substantially leveled by the beginning of the Satkinskian. The predominance of mainly terrigenous deposits during the last stages in the evolution of the Early Riphean Volga-Urals basin was most likely caused by substantial reduction in the area of the basin's aquatory and transformation of an extensive, flat epicontinental marine water basin into a lakelike basin of substantially smaller size.

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TECHNIQUE

INTEGRATED APPLICATION OF PALYNOLOGICAL, GEOCHEMICAL, AND MINERALOGICAL DATA FOR IDENTIFICATION OF PALEOCLIMATOLOGICAL EVENTS IN REGIONS OF TERRIGENOUS SEDIMENTATION

V. R. Tumanov, L. P. Zharikova, and S. A. Safarova

UDC 550.4:552.08

There is an urgent need for climatostratigraphic studies of the Cenozoic era for the purposes of geological mapping, the search for mineral products, and ecological and climatological forecasting. The greater the number of independent indicators of the paleoclimatological setting that are taken into account, the more reliable will be the results of such studies. Below we consider whether it is possible to determine paleoclimatological events on the basis of a group of standard palynological, chemical, and mineralogical analyses.

An extremely large number of components of the sediment has been studied, up to the dozens and sometimes a few hundred. To get a comprehensive idea of such information it is best to undertake a convolution of the information and represent it in the form of a bounded set of numbers coupled to the lithostratigraphic columns. Dimensionless and comparable numerical indicators of the paleoclimate obtained by entirely independent methods could probably be determined by arranging the lists of the investigated components in terms of whether they relate to moist and warm environments or, alternatively, to dry and cold environments, and dividing the sum (or product) of the contents of the leading terms of these biological, geochemical, and mineralogical series.

Ratios of products would more correctly express the variations of the indicators with respect to profile than would ratios of sums, since in multiplication and division the components occur as "equally justified," independently of the classes of contents, whereas if the contents of at least one component is zero, the result will be undefined, and then it would be more correct to use as the indicators the ratios of the sums of the contents of the components.

PALYNOLOGICAL INDICATORS OF PALEOCLIMATES

Lists of spores and pollen are ordered with respect to two trends in the indicator space, the temperature trend and the water-moisture trend. The climatological and ecological membership of the palynological taxons is established by comparing them with contemporary flora [1, 3, 12, 13]. The ratio of the sum of the spores and pollens of relative thermophytes to the sum of the spores and pollens of cold-resistant plants is taken as the indicator of thermophilicity of the flora. By the hydro + hydrophilicity indicator we understand the ratio of the sums of the spores and pollens of cold-resistant hygrophytes and aquatic plants to the sum of the spores and pollens of the xerophytes. We believe that the product of these ratios may serve as a generalized palynological indicator of the temperature and moisture conditions of the paleoclimates.

In determining paleoclimates on the basis of the palynological indicators errors may be encountered due mainly to difficulties in spore and pollen diagnosis. These errors are often limited to the names of the genera or even families of plants that combine species with different temperature and moisture living conditions. It is very difficult to take into account the selective destruction of different groups of spores and pollens in the soil and in the diagenesis of sediment or the grade distribution of the palynological residues in accordance with their aereo- and hydrodynamic forms in sedimentation [12]. The more ancient the deposit, the greater the proportion of plant residues present in the deposit whose ecology is unknown, while in the case of spores and pollens determined in artificial classifications, until recently it has been

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An extremely large number of components of the sediment has been studied, up to the dozens and sometimes a few hundred. To get a comprehensive idea of such information it is best to undertake a convolution of the information and represent it in the form of a bounded set of numbers coupled to the lithostratigraphic columns. Dimensionless and comparable numerical indicators of the paleoclimate obtained by entirely independent methods could probably be determined by arranging the lists of the investigated components in terms of whether they relate to moist and warm environments or, alternatively, to dry and cold environments, and dividing the sum (or product) of the contents of the leading terms of these biological, geochemical, and mineralogical series.

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In determining paleoclimates on the basis of the palynological indicators errors may be encountered due mainly to difficulties in spore and pollen diagnosis. These errors are often limited to the names of the genera or even families of plants that combine species with different temperature and moisture living conditions. It is very difficult to take into account the selective destruction of different groups of spores and pollens in the soil and in the diagenesis of sediment or the grade distribution of the palynological residues in accordance with their aereo- and hydrodynamic forms in sedimentation [12]. The more ancient the deposit, the greater the proportion of plant residues present in the deposit whose ecology is unknown, while in the case of spores and pollens determined in artificial classifications, until recently it has been

TABLE 1. Zonality of Weathering Processes and Products [6]

Weathering Zone	Stability Group	Assemblage of Relic Minerals
Ochre and Oxides	V	Relics of zirconium, rutile, tourmaline, quartz, graphite
Kaolinitic	IV	Rutile, anatase, cassiterite, monazite, tourmaline, leucoxene, graphite, quartz with traces of dissolution, zirconium, molacon, ilmenite, corundum (?), disthen (?)
Hydromica-Kaolinitic	III	Disthene, staurolite, sillimanite, almandine, microcline, andalusite, minerals of groups IV and V
	II	Muskovite, sphene, epidote, zoisite, pennine, clinocllore, tremolite, actinolite, orthoclase, acidic plagioclases, aegirine, apatite (?), biotite, minerals of groups III and IV
Hydromica, Disintegration	I	Common hornblende, apatite, grossularite, medium and basic plagioclases, magnetite, biotite, augite, diopside, nepheline, ferrichlorites, glauconite, volcanic glass, montmorillonite, organic matter, ferric sulphides, and minerals of groups II, III, and IV

believed that it would not be reasonable to draw analogies to contemporary floras [8, 17]. It is clear that the various problems that stand in the way of determining the paleoclimates on the basis of palynological data are fewer in number, the more homogeneous the lithology of the strata that are being studied.

EVALUATION OF GEOCHEMICAL INDICATORS OF THE HUMIDITY ARIDITY OF PALEOCLIMATES

Series of chemical elements (or their components), from elements that are low mobility to those that are high mobility in conditions under which weathering crusts form and ordered in accordance with the stability coefficient are used to evaluate the geochemical humidity indicator of paleoclimates. (The stability coefficient is equal to the ratio of the content of an element per unit of volume in the most highly weathered rock to its content in the same volume of the initial rock.) The following mobility series is known [10] for the weathering crusts of basic rock under high-temperature and high-moisture conditions: Al, Fe, Ti, Ga, Zr (1.0-0.7), Cr, V (0.7-0.5), Si, Ni, Zn, Pb, Cu (0.5-0.3), K, Na, Mn, Ca, Mg (0.3-0.006). The analogous weathering series for the weathering crusts of the ultrabasites is Ti, Al, Cr, Fe, Mn, Co, Ni, Si, Ca, and Mg, and for the granitoids Al, Ti (1), Si, Fe (0.6-0.3), Mg, Ca, K, Na (0.3-0.02) [11].

It has been suggested [15] that the factor $(Al \cdot Ti)^2 / Ca \cdot Na \cdot Mg \cdot K$, qualitatively balanced so that the basicity (Ca, Mg) — sialicity (Na, K) factor is mutually suppressive while the weathering factors are underscored, be used as a generalized indicator of the extent to which the rock has been affected by chemical weathering.

One drawback of the indicator is the fact that it cannot distinguish the low-temperature desert and polar sedimentation environments in which the primordial contents of Ca, Mg, and K have been preserved in the autochthonous grains, from the high-temperature arid environments in which these chemical components accumulate even in the autochthonous constituent of deposits. Moreover, the high content of Ti and, to a lesser degree, of Al, may be related not only to weathering of the terrigenous components, but also their basicity.

EVALUATION OF MINERALOGICAL INDICATORS OF HUMIDITY OF PALEOCLIMATES

The allochthonous mineral components of terrigenous sediment under the conditions of chemical weathering range from the stable to the unstable in the following series [11]: quartz — muscovite — orthoclase, microcline — albite — biotite, oligoclase — amphibole hornblende, andesine — pyroxenes, labradorite — olivine, bytownite.

TABLE 2. Variation of Composition of Terrigenous Minerals of Sandy-Siltstone Fractions of Contemporary Alluvium [7]

Type of variation	Minerals whose downstream content	
	is increasing	is decreasing
Distinctive	Zirconium Rutile Sphene Leucosene Sillimanite	Granates Monoclinal Pyroxenes Microcline
Less distinctive	Ilmenite Disthene Andaluzite Pyrite Zoisite (?) Tourmaline (?) Glauconite (light fraction)	Rhombic Pyroxenes Amphibole Hornblende Chloritoid Chlorite Apatite Rock fragments (heavy and light fractions) Orthoclase
Unclear	Epidote Alkali Amphibole Hornblende Mica Magnetite Fragments of Siliceous Rocks	

The ratio (quartz + feldspar)/(amphibole hornblende + pyroxene) or the analogous ratios of the sum of the stable minerals to the sum of the unstable minerals may be taken as the indicator of the mineral age of a deposit. The drawback of such indicators – that the minerals in the numerator belong to the light fractions of the sediment, while the minerals in the denominator to the heavy fractions – and the fact that basicity governs whether a mineral occurs in the light or the heavy fractions, represents the sialicity of the source.

In terms of their confinement to climatic belts, finely dispersed minerals in sediment from the polar to the equatorial zone are arranged in the same order as in the profile of weathering crusts thus: chlorites, hydromica, montmorillonite – kaolinite – bauxite minerals. A climatic indicator that is little affected by the factor or by noise is the ratio (kaolinite + bauxite minerals)/(chlorites + hydromica), though the quantitative determination of these minerals represents an extremely time-consuming task.

In actual practice investigators focus on grains of the dimension of silt and sand. Those which are opposite in terms of resistance to the effects of weathering (Table 1) and, at the same time, are similar in terms of stability in the areas of seas and river flows are the most interesting of these size grains. The relatively more stable minerals are [6] zirconium, rutile, tourmaline, monacite, sphene, ilmenite, magnetite, quartz, siliceous fragments, mica, epidote (?); the relatively less stable minerals are pyroxene, amphibole hornblende, granates (?), apatite, microcline, and plagioclases. Table 2 presents data showing how the compositions vary in riverine flows. Judging on the basis of these data, the ilmenite/magnetite ratio would seem to be the best index of weathering, understood as a function of climate, while the zirconium/granate ratio, or analogous ratios of minerals that are stable in humid conditions to minerals that are unstable under these conditions are somewhat worse. But general laws governing the distribution of minerals in rocks of sources of ablation (Table 3) as well as their regional distribution features must be taken into account, since the composition of a source of ablation may entirely conceal the climatic factor.

INTEGRATED APPLICATION OF PALYNOLGICAL, GEOCHEMICAL, AND MINERALOGIC DATA TO DETECT PALEOCLIMATOLOGICAL EVENTS

Example 1. As a test we selected the most completed studied example of a stratigraphic [2, 4, 9, 16, 17] Paleocene and Neogene section from Yakutia taken from borehole 1 in the undercurrent of the River Kolyma (Fig. 1).

TABLE 3. Assemblages of Heavy Minerals and Initial Rocks [14]

Assemblage	Source
Apatite, biotite, brookite, hornblende, monazite, muskovite, rutile, titanite, (rose) tourmaline, zirconium	Igneous persilicic rocks
Cassiterite, dumourtierite, fluorite, granate, monazite, muskovite, topaz, (blue) tourmaline, wolframite, xenotime	Granitic permatites
Andalusite, chondrodite, corundum, granate, amber mica, staurolite, topaz, vesuvianite, wollastonite, zoisite	Contact metamorphic rocks
Barite, iron ores, leucoxene, rutile, tourmaline (rounded grains), zirconium (rounded grains)	Reworked sediment (sedimentary rocks)

Its Lower Paleogene to Middle Miocene part is represented by lacustrine, rarely pelagic, siltstones, clays, sands, and lignite, while the Upper Upper Miocene–Pliocene part, mainly by alluvial pebbles and sand. Closely situated sources of fragmental material of the basic composition have been established [15] for the lower part of the section, while more highly dispersed sources formed by granitoids are found in the upper part. The section is situated near the boundary of open deciduous forests (dwarf birch thickets, heather, green moss, and lichens) with the tundra.

From the standpoint just outlined, we undertook to analyze the primary records of spore and pollen analyses that have served as a basis for previously published conclusions (cf. [4, 16, 17] regarding the stages and sequence of variations in the plant cover and climate in the northeast portion of Yakutia).

The obvious thermophilic forms analogs of which are known in the contemporary tropics and subtropical regions include *Taxodiaceae*, *Glyptostrobus*, *Comptonia*, *Ulmoideipites*, and the more rarely encountered *Menispermaceae*, *Magnoliaceae*, *Altingiaceae*, *Mytaceae*, *Hamamelidaceae*, *Oleaceae*, certain genera from the families *Juglandaceae* – *Alfaroa*, *Oreamunoa*, *Engelhardtia*, *Eucommiaceae*, *Pistaciaceae*, and *Celtidaceae*, in all over 100 taxons characterizing the climatic optima of the Paleocene and Eocene era of northern Yakutia.

Among the mid- and sub-tropic and southern moderate families and genera that are found in the data for the regions to be thermophytes beginning in the Oligocene we may cite the coniferous *Abies*, *Picea*, *Tsuga*, *Keteleeria*, and *Cedrus*, genera of the family *Cupressaceae*, as well as the deciduous *Fagus*, *Castanea*, *Quercus*, *Juglans*, and *Pterocarya* along with other representatives of the "Turgai" flora and of the grasses, *Amarillidaceae*.

Of the cold-resistant plants we may cite *Betula* with small pollen, the brushwood *Salix*, of the grasses, *Artemisia*, *Cyperaceae*, *Cramineae*, of the sporophytes *Hepaticae*, *Sphagnum*, *Bryales*, and more rarely, *Dycranaceae*, *Meesia*, *Licopodium alpinum*, *L. sect. selago*, *L. cimosum*, and *Selaginella sibirica*.

We may list among the water- and moisture-loving plants in this section *Taxodium*, *Glyptostrobus*, *Trema*, *Chaetachme*, *Nyssa*, *Traps*, *Polygonum persicarya*, *P. laxmanii*, *P. triptocarpum*, *Lentibulariaceae*, *Alismataceae*, *Sagittaria*, *Hydrocharitaceae*, *Potamogeton*, *Liliaceae* (?), *Sparganiaceae*, *Typhaceae*, *Sphagnum*, and *Bryales*. Since these forms are absent from a significant proportion of the specimens, taxons that cannot be subsumed among plants that are confined to moist conditions with the same degree of certainty, but are more widespread, such as *Betula* with small pollen and *Ericales*, as well as *Podocarpus*, *Dacridium*, *Nuphar*, *Nymphaeaceae*, *Pterocarya*, *Polygonatum*, *Equisetum*, and *Osmunda*, may also be included among the hydrophytic plants.

Among the xerophytic plants we may include *Juniperus*, *Ephedra*, *Myrica*, *Comptonia*, *Cornaceae*, *Chenopodiaceae*, *Plumbaginaceae*, and *Artemisia*. The pollen of these plants is encountered in small quantities in a limited number of samples, and therefore a list of the relative xerophytic plants was enlarged at the expense of genera and species of *Pinaceae* and *Cupressaceae*.

Curve I for the thermophilicity indicator illustrates how the indicator decreases cyclically from the Paleocene to the Upper Oligocene by a factor of 10^4 and then increases by 10 or 10^2 in the period from the Lower to the Middle Miocene followed by a new cyclic decrease by 10^3 in the Upper Miocene and the Lower Pliocene. This cyclic behavior is entirely in agreement with generally accepted notions of the direction of variations in the corresponding paleoclimates [8].

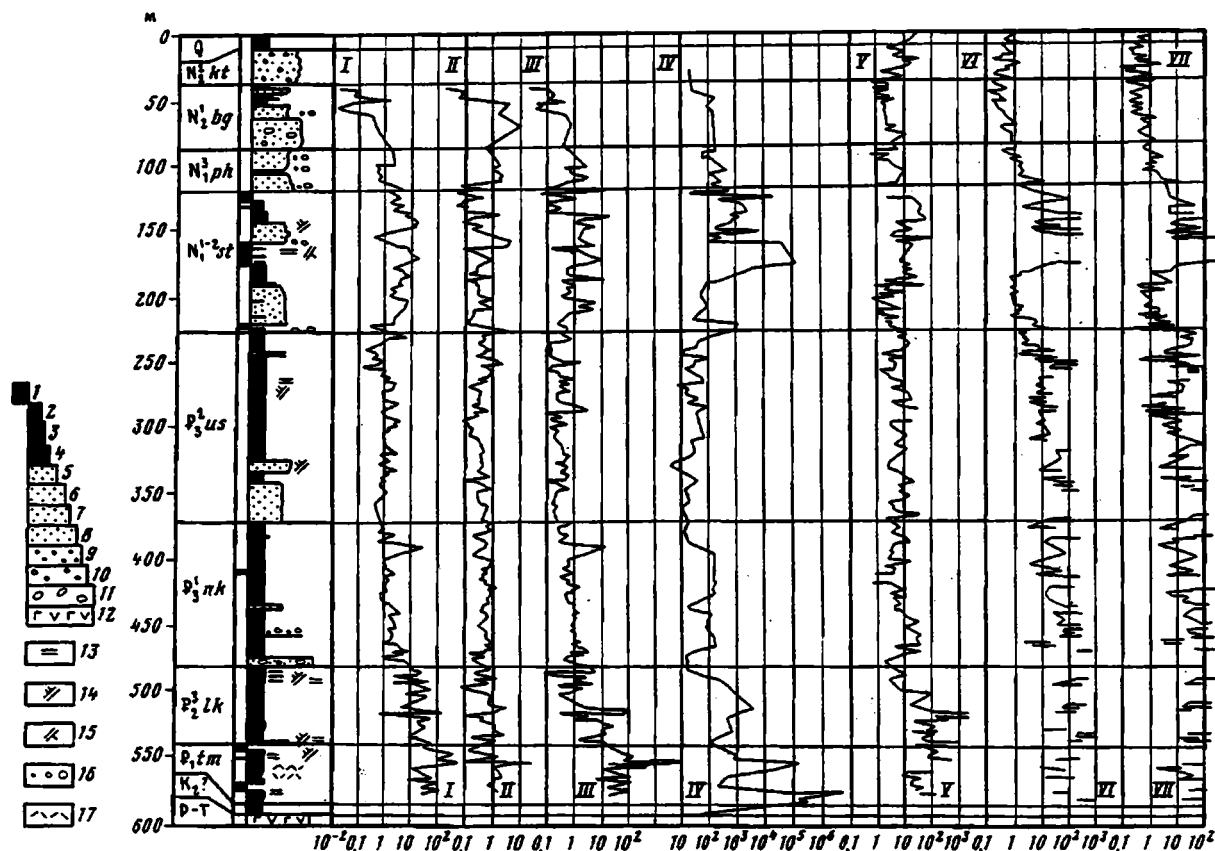


Fig. 1. Curves of paleoclimatic indicators in the section of borehole 1. (1) lignite; (2) clays; (3) and (4) silts ((3) fine-grained, (4) coarse-grained); (5)-(8) fine-, close-, medium-, and coarse-grained, respectively, sand; (9) gravel; (10) coarse gravel; (11) cobble round-stones; (12) andesite-basalt, basalt, and tuff; (13)-(15) bedding ((13) horizontal; (14) cross; (15) sinuous); (16) plant detritus; (17) fossil soils. Curve I: ratios of the sum of thermophyte spores and pollens to the sum of the spores and pollens of cold-resistant plants. Curve II: ratios of the sum of the spores and pollens of hydro- and hygrophytes to the sum of the spores and pollens of xerophytes. Curve III: products of the first two ratios (generalized indicator of the temperature and moisture conditions). Curve IV: indicators of chemical age ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2)^2 : (\text{CaO} \cdot \text{MgO} \cdot \text{K}_2\text{O} \cdot \text{Na}_2\text{O})$. Curve V: ratio of zirconium to granates; curve VI: ratios of the sum of magnetite and ilmenite to the sum of amphibole hornblende and pyroxenes; curve VII: ratios of the sum of quartz and feldspar to the sum of amphibole hornblende and pyroxenes. Q, Quaternary deposits; N_2^1kt , Upper Pliocene, Kutuyakh suite; N_2^1bg , Lower Pliocene, Begunov suite; N_1^3ph , Upper Miocene, Pokhod suite; N_1^1-2st , Lower to Middle Miocene, undivided rocks, Stadukh suite; P_3^1us , Upper Oligocene, Ust'-Omolon suite; P_3^1nk , Lower Oligocene, Lower Kolyma suite; P_2^1lk , Upper Eocene, Lakeev suite; P_1tm , Paleocene, Timkin suite; K_2 (?), Upper Crustacean (?), weathering crust; P - T, nonarticulated Permian and Triassic effusive rocks.

Curve II for the hydro- and hygrophyllicity indicator demonstrates how this indicator varies by a factor 10^2 and rarely 10^3 with its greatest values in the Paleocene and the Upper Miocene through the Lower Pliocene, and its least values in the Upper Oligocene, in the Lower and Middle Miocene and in the very upper parts of the Lower Pliocene. These are new data. The values of the thermophyllicity indicators and of the hydro- and hygrophyllicity indicator are in positive correlation across the suite in a comparison ($r_{I,II} = 0.80 \pm 0.27$).

The curve for the generalized indicator of the temperature and moisture conditions of the paleoclimates (curve III) shows how its modulus varies from figures in the hundreds and thousands in the Paleocene to several dozen and several tenths in the Eocene, gradually decreasing from units to tenths in the Oligocene, sharply varying with an overall increase in values in the Lower to the Middle Miocene and again decreasing from units to hundredths in the Upper Miocene to the Lower Pliocene. The general spread of the values of the indicator amounts to six orders of magnitude. The correlation

coefficient found from a comparison of indicators III and I in the suite amounts to 0.85 ± 0.24 , and of indicators III and II, 0.82 ± 0.25 .

The thermophilicity curve I and, to an even greater degree, the multiplicative curve describing the temperature and moisture conditions under which the paleoflora existed (curve III) are in good agreement with the curve describing the indicator of geochemical age of the deposits (curve IV; cf. Fig. 1). Resemblance between the variations of the indicators is established quite unambiguously in a comparison of the indicators across the suite ($r_{I,IV} = 0.85 \pm 0.24$; $r_{II,IV} = 0.75 \pm 0.30$; $r_{III,IV} = 0.86 \pm 0.23$) for the Paleocene and the Eocene, and the curves are seen to coincide for particular extremal peaks and minima. As expected, the analogous curves of the palynological indicator of temperature and moisture conditions are higher than the other curves. The geochemical age curve is more closely connected to the lithology of the particular period than are the curves drawn from the palynological data. Layers of kaolinitic clays with elevated pollen content determined in the artificial classifications as *Triatriopollenites* and *Tricolporopollenites* correspond to the intervals of maximal chemical age. There is thus a reliable basis for suggesting that the conditions under which these plants grew were moist and hot, corresponding to the warm subtropics or even the tropics. White pod-bearing allits (the spores and pollen of these plants have not been preserved) correspond to the highest peak of values of the chemical age curve for the Paleocene at a depth of 576-577 m.

The fact that the curves of the palynological and the geochemical indicators do not coincide in their details may be explained by the different steps used in determining the indicators and by different sampling sites for different types of analyses, the difficulties encountered in attempting to determine the temperature and moisture characteristics on the basis of the palynographic data, and, finally, the fact that the very correspondence between the indicators cannot be said to be absolutely certain inasmuch as these indicators have not been completely determined. The objectivity of the paleoclimatic variations helps in making use of data from mineralogical analysis.

We have available mineralogical data from past studies both on the heavy as well as the light fractions of deposits uncovered in borehole 1. Ilmenite and magnetite from the analyses appear together in the records, and therefore it is not possible to analyze their ratio. The magnitude of the zirconium-granate ratio depends on the paleoclimate, the duration and distance over which the allochthonous material was transported, and the composition of the ablation source. In the section that was studied the climate factor is decisive. This is proved by the reliable positive correlation between the variations of the suite indicators thermohydrophilicity + hydrophilicity of the flora and the chemical age of the deposit, on the one hand, with the variations in the modulus of the zirconium/granate ratio in the interval of the section from the Eocene to the Pliocene ($r_{III,V} = 0.71 \pm 0.31$; $r_{IV,V} = 0.66 \pm 0.33$), on the other hand. Granate is absent from the Paleocene layers with maximal chemical age, and the ratios of the zirconium/granate ratio are indefinitely high and were not taken into account in estimating the arithmetic mean, which is therefore understated.

Important paleoclimatic information is provided by analysis of the variations in the two ratios (ilmenite + magnetite)/(amphibole hornblende + pyroxene) and (quartz + feldspar)/(amphibole hornblende + pyroxene). Obviously, if the corresponding curves (curves VI and VII; cf. Fig. 1) are similar and are in agreement with the chemical age curve, their peaks and minima will be connected not with the basicity – sialicity of the source nor with the mechanical and hydrodynamic properties of the grains, but instead with their degree of weathering caused by the effects of the paleoclimate which they exhibit. It has been established that the geochemical age curves (curve IV) and the ratio (ilmenite + magnetite)/(amphibole hornblende + pyroxene) are especially close in the Neogene interval of the section, particularly in areas corresponding to the Early and Medium Miocene climatic optimum, a result that once again confirms the reliability of our identification of this paleoclimatic event. It is also obvious that if the role of the sialic component in the sediment were increasing from below upwards [15], whereas the value of the indicator (quartz + feldspar)/(amphibole hornblende + pyroxene) were decreasing, the cause would lie in a more severe paleoclimate. Such a picture is observed in curve VII in the supra-optimal Neogene part of the curve.

The fact that curves VI and VII for the Upper Oligocene are mirror images of each other illustrates the inverse correlation between the two curves and the influence of the sialic source of ablation on curve VII and on the overall appearance of curve VI, the paleoclimate factor.

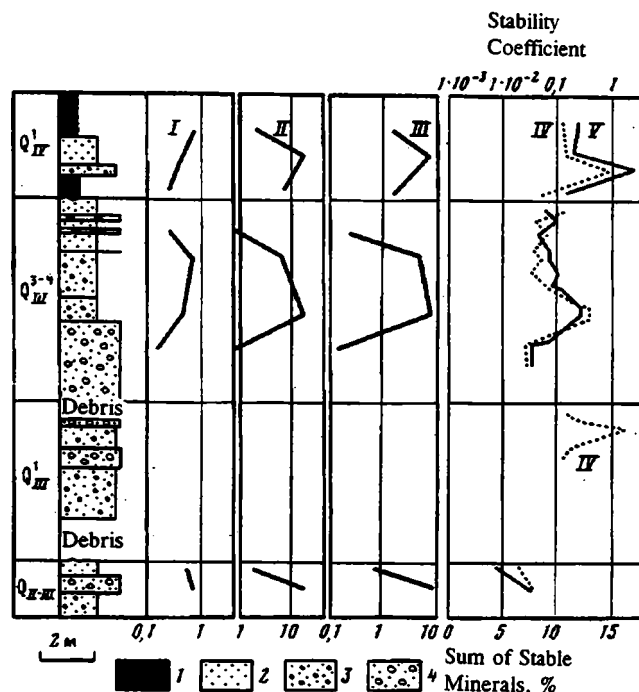


Fig. 2. Curves of the paleoclimatic indicators of alluvial deposits in the basins of the headwaters of the River Yan. (1) sandy loam; (2) sands; (3) gravel; (4) coarse gravel. Curve I: ratios of the sum of thermophyte spores and pollens to the sum of the spores and pollens of cold-resistant plants. Curve II: ratios of the sum of the spores and pollens of hydro- and hygrophytes to the sum of the spores and pollens of xerophytes. Curve III: products of the first two ratios. Curve IV: sums of zirconium + rutile + ilmenite + leucoxene. Curve V: ratio of the sum of the contents of these minerals to their contents in an artificial feldspar concentrate. Q_{IV}^1 , Q_{III}^{3-4} , Q_{II}^1 , Q_{I-II} , deposits corresponding to curves I-IV for the terraces above the floodplain.

The discordance between curves VI and VII, on the one hand, and curves III, IV, and V, on the other, which is observed lower down across the section demonstrates damping of the climatic factor by mechanical factors, the composition of the source and, consequently, the unsuitability of the moduli of curves VI and VII for explaining the paleoclimate in the Paleogene interval of this section. Amphibole hornblende and pyroxene are absent from the essentially kaolinite Paleogene deposits, and of the accessory minerals only ilmenite-magnetite is preserved. This limits the range of applicability of those indicators whose denominator contains the femic rock-forming minerals.

Example 2. Figure 2 shows the lithology and palynological and mineralogical data for the Quaternary alluvial terraces in the headwaters of the River Yan. The region is located in a zone of northern mountainous taiga whose arborescent stage is represented by larch, bushes and heather, and dwarf arctic birches, while the soli is covered with lichen and green moss. The principal relative thermophytes in this example are all the coniferous trees, except for *Larix* and *Pinus pumila*, and all the birches, except for the bush *Betula*. Among the cold-resistant plants we may cite *Pinus pumila*, *Betula middendorffii*, *B. exilis*, and certain other forms with small pollen (excluding *B. fruticosa*) and certain grasses and green mosses. We consider as relative hygrophytes all the Altai birches (*B. fruticosa*), small birch trees (in this section they are accompanied by Altai birches and moss and are in inverse correlation with pine trees), brownish moss, as well as rare forms of *Polygonum tripterocarpum*, *P. laxmanii*, and *Equisetum*. The community of relative xerophytes includes all the pine trees, Siberian ground-pines, and, in a subordinate role, certain grasses of meadowland-steppe assemblages.

In artificial concentrates washed off from terraces, of the stable minerals only zirconium, rutile, ilmenite, and leucoxene are found, and of the unstable minerals, only feldspar. The ratio of the sum of the accessory minerals resistant to weathering to feldspar (cf. Fig. 2, curve IV) reveals a weak negative correlation with the thermophyllicity indicator (-0.34 ± 0.35), a weak positive correlation with the hydrophyllicity indicator (-0.37 ± 0.18), and the closest correlation with the indicator of the temperature and moisture conditions of the paleoclimates (0.53 ± 0.32). No spores or pollen are

found in the Q_{III}^1 deposits, though from the high content of the sum of the stable minerals it may be assumed that they were actually formed in a period of relative increasing warmth.

We are unable to present convincing examples illustrating positive correlation between the indicator of the temperature and moisture conditions and the ilmenite/magnetite ratio, despite the fact that we have reviewed archival data on dozens of sections of the continental shelf in Yakutia from the Cenozoic. In certain sections only magnetite was found (near Phanerozoic granitoid blocks), while in others ilmenite (if basic igneous rock predominated in the ablation source), while in a third group of sections both minerals were found, though a positive correlation with the thermohydrophilicity indicator for the paleo-flora was noted only in portions of the sections, this correlation breaking down probably due to variations in the direction of the ablation. The ratio (ilmenite + leucoxene + fragmental limonite)/magnetite correlates with the palynological indicator of the temperature and moisture conditions somewhat more closely but the relation between them nevertheless remains uncertain.

* * *

At the start of the Timkin period in the Paleocene (interval in the section below the first layer of coal from the bottom) the kaolinite clays and allites lacking spores and pollens were probably formed in a subtropical environment that was warmer and moister than that predicted by the palynological data [8], i.e., moderate in temperature, that is, a subtropical environment.

In occasional blossoming of triatripollentes flora the climate was nearly as warm and moist as during the build-up of allites at the start of the Timkin period.

Accumulation of plant residue in reservoirs facilitated the periodic destruction of subtropical forests and replacement of the subtropical environment by one with moderate temperatures due to sharp relative coolings.

In the Lakeev period of the Late Eocene, the expression of the moderate temperature climate conditions [8] was maximal in the middle of the period. In terms of characteristics, this climate optimum corresponds to the background climate of the Paleocene.

In the Lower Kolym (Early Oligocene) and Ust'-Omolon (Late Oligocene) periods the climate varied cyclically, tending to an increasingly moderately colder environment with relatively stable humidity.

As in the Paleocene, in the Stadukh period of the Early to Middle Miocene abrupt variations in the temperature and moisture characteristics of the paleoclimate occurred that were also of considerable amplitude. In the clearly expressed maximal climate optimum that occurred in individual episodes, the increase in the temperature and moisture coincided and processes of chemical weathering reached the same degree of intensity as in the last of the Paleocene optima. During this time the thickest of the layers of plant detritus was laid down, and this subsequently metamorphosed into coal. The formation of other coal beds may be attributed to occasional drops in the temperature and to variable, mainly low, humidity.

Plant communities of the Stadukhin optima resemble those in central Ukraine and the northern Caucasus where the mean-annual temperatures are in the range 12-13°C and the total precipitation in the range 500-1000 mm.

In the Later Miocene to the Early Pliocene orogenesis occurred in regions of ablation together with strong cooling and at first an increase, and, at the end of the Begunov period, a very profound drop in moisture, and replacement of moderate cold landscapes by taiga and tundra.

Analysis of the ratios of the extreme terms of the lists of spores and pollen, ordered in terms of the paleo-ecological indicators, makes it possible to estimate the relative variations in the temperature and moisture of the paleoclimates based on dimensionless numerical indicators. These indicators may serve as numerical and graphical models of the climate variations, in particular of the range, differentiation, and cyclicity of these variations. On the basis of individual parts of the models, the models may be approximately "coupled" to contemporary climate environments with known temperature and moisture characteristics.

The ratios of the extreme terms of the series of components, ordered by alternative attributes, reflect some of the principal characteristics of the paleoclimatic events far more graphically and concretely than do the curves expressing the contents of each of the components or sums of these components that have been used until now, though they cannot replace the most elementary numerical data.

Variations in the geochemical age of the rocks and, in individual sections and parts of sections, variations in the ratios of minerals that are resistant to weathering to the minerals that are not are in good agreement with variations in the palynological indicator of the temperature and moisture conditions of the paleoclimates.

We recommend that the rationale for selection of the indicators that is proposed here be introduced into geological mapping and paleoclimatic investigations.

The reliability of the conclusions regarding the paleoclimates that have been presented here may be improved if in the interpretation of the scheme proposed here data on other groups of microfossils and chemical components of organic matter are made use of.

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